PB83-207647

At-Sea Incineration of PCB-Containing Wastes Onboard the M/T VULCANUS

TRW, Inc., Redondo Beach, CA

Prepared for

Industrial Environmental Research Lab.
Research Triangle Park, NC

Apr 83

U.S. Department of Commerce
National Technical Information Service
NTIS

PB83-207647

EPA-600/7-83-024
April 1983

AT-SEA INCINERATION OF PCB-CONTAINING WASTES ONBOARD THE M/T VULCANUS

by

D.G. Ackerman, J.F. McGaughey, and D.E. Wagoner
TRW Inc., Energy and Environmental Division
One Space Park
Redondo Beach, CA 90278

Contract No. 68-02-3174, Work Assignment No. 103

Task Officer: M.D. Jackson

Industrial Environmental Research Laboratory
Office of Environmental Engineering and Technology
Research Triangle Park, NC 27711

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

Prepared for:

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Washington, D.C. 20460

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/7-83-024	2.	3. RECIPIENT'S ACCESSION NO. PB83 207647
4. TITLE AND SUBTITLE At-sea Incineration of PCB-containing Wastes Onboard the M/T VULCANUS		5. REPORT DATE April 1983
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) D. G. Ackerman, J. F. McGaughey, and D. E. Wagoner		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS TRW, Inc. One Space Park Redondo Beach, California 90278		10. PROGRAM ELEMENT NO.
		11. CONTRACT/GRANT NO. 68-02-3174, Task 103
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development Industrial Environmental Research Laboratory Research Triangle Park, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED Final; 8/82 - 1/83
		14. SPONSORING AGENCY CODE EPA/600/13

15. SUPPLEMENTARY NOTES IERL-RTP project officer is Merrill D. Jackson, Mail Drop 62, 919/541-2559.

16. ABSTRACT The report describes tests during the incineration-at-sea of a shipload of polychlorinated biphenyls (PCBs) onboard the M/T VULCANUS, during August 1982 in the Gulf of Mexico. A standard EPA-specified sampling train was used to acquire samples of the effluent combustion gases. A fixed-position water-cooled probe, in the starboard incinerator, directed stack gas to the train. Ten tests were performed. Samples of the waste were also taken during each test. Samples were analyzed on land for PCBs, chlorobenzenes, tetrachlorodibenzofurans (TCDFs), and tetrachlorodibenzo-p-dioxins (TCDDs). Other test related activities included wipe-sampling and onboard analysis of these samples, acquisition of samples of work space air in the incineration control room and the dining room, and acquisition of pertinent process related data. The various measures of performance met or exceeded requirements of the permit. Incinerator walls averaged 1303 C, oxygen 10.1 percent, carbon dioxide 9.1 percent, carbon monoxide 8 ppm, combustion efficiency 99.99 percent, and destruction efficiencies greater than 99.99 percent for PCBs and chlorobenzenes and greater than 99.9 percent for TCDFs.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Pollution	Incinerators	Pollution Control	13B	
Chlorine Aromatic Compounds	Waste Treatment	Stationary Sources		
	Decontamination	Polychlorinated Biphenyls	07C	14G
Biphenyl				
Liquids		At-sea Incineration	07D	
Waste Disposal		Waste Collection	15E	

18. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 287
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE

EPA Form 2220-1 (9-73)

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

ABSTRACT

This report describes the testing that was performed during the incineration at sea of 3,523 metric tons of wastes containing polychlorinated biphenyls (PCBs) onboard the incineration ship M/T VULCANUS. The incineration took place during the period 15-31 August 1982 in the Gulf Coast incineration site, an area in the Gulf of Mexico designated by the U.S. Environmental Protection Agency (EPA) for such purposes. One shipload was burned during this test project under EPA-issued research permit number HQ-81-002. Chemical Waste Management (CWM), Inc., Oak Brook, IL, and Ocean Combustion Service (OCS) BV, Rotterdam, The Netherlands, were the permittees. OCS operates the M/T VULCANUS and is a wholly owned subsidiary of CWM which supplied the waste.

EPA contracted with the Energy and Environmental Division of TRW Inc., Redondo Beach, CA, to sample and monitor the incineration process and analyze the samples in order to determine compliance with the operating and safety requirements of the permit. A representative from EPA, (the Task Officer) was onboard during the testing, and a technician-employee of EPA assisted the TRW Test Team.

A standard EPA-specified sampling train was used to acquire samples of the effluent combustion gases. A fixed-position, water-cooled probe was mounted in the starboard incinerator and directed stack gas to the train. A total of 10 tests were performed. Samples of the waste were also taken during each test. Samples thus acquired were analyzed on land for PCBs and chlorobenzenes by TRW. Portions of the same samples were analyzed for tetrachlorodibenzofurans (TCDFs) and tetrachlorodibenzo-p-dioxins (TCDDs) by personnel of the Chemistry Department of the University of Nebraska, Lincoln, NB, and the Environmental Monitoring and Systems Laboratory of EPA, Research Triangle Park, NC (EMSL-RTP).

Other test-related activities included wipe-sampling and onboard analysis of these samples to determine compliance with the health and safety plan, acquisition of samples of work space air in the incineration control room and the dining room, and acquisition of pertinent process-related data (e.g., temperatures in the incinerators, feed rates of waste, and concentrations of carbon dioxide (CO_2), oxygen, (O_2), and carbon monoxide (CO) in the combustion gas).

The various measures of performance met or exceeded requirements of the permit. Incinerator wall temperatures averaged 1303°C, oxygen 10.1 percent, carbon dioxide 9.1 percent, carbon monoxide 8 ppm, combustion efficiency 99.99 percent, and destruction efficiencies greater than 99.99 percent for PCBs and chlorobenzenes and greater than 99.9 percent for TCDFs.

This report was submitted in fulfillment of Work Assignment No. 103 of Contract No. 68-01-3174 by the Energy and Environmental Division of TRW Inc. under sponsorship of the U.S. Environmental Protection Agency. This report covers work from 2 August 1982 to 2 January 1983.

CONTENTS

Disclaimer ii

Abstract iii

Figures. viii

Tables ix

Acknowledgements xi

1. INTRODUCTION AND SUMMARY 1
    1.1 Introduction. 1
    1.2 Summary of Results 2
2. DESCRIPTION OF THE M/T VULCANUS. 5
    2.1 General Layout of the Vessel. 5
    2.2 Tank and Pumps. 5
    2.3 Incineration System 8
    2.4 Measurement of Waste Flow Rate. 10
    2.5 Thermal Measurements. 10
    2.6 Emergency Automatic Waste Shutoff 11
    2.7 Combustion Gas Monitoring System. 13
3. TEST OPERATIONS. 16
    3.1 Sampling of the Stack Gas 16
        3.1.1 Equipment. 16
        3.1.2 Operations and Procedures. 22
    3.2 Contamination Control Sampling. 26
    3.3 Other Samples and Measurements. 28
        3.3.1 Sampling of the Waste. 28
        3.3.2 Sampling of Work-Space Air 28
        3.3.3 Monitoring 28

CONTENTS (Continued)

4. TEST RESULTS 29
  4.1 Description of Waste. 29
  4.2 Waste Feed Rates. 30
  4.3 Volumes of Stack Gas Sampled. 32
  4.4 Composition of the Combustion Effluent. 32
  4.5 Temperatures and Residence Times. 34
  4.6 Safety and Personnel Protection 36
    4.6.1 Design of the Personnel Protection Plan. 36
    4.6.2 Implementation of the Personnel Protection Plan. . 39
    4.6.3 Results of Analyses of Wipe-Samples. 40
    4.6.4 Results of Analyses of Work Space Air Samples . . 42
5. ANALYTICAL RESULTS 43
  5.1 Introduction. 43
  5.2 Reagents and Chemicals. 45
    5.2.1 Solvents 45
    5.2.2 Chemicals. 45
  5.3 Sample Preparation. 45
    5.3.1 Impinger Contents (Container No. 1). 46
    5.3.2 Hexane and Acetone Rinses of Probe, Teflon® Line, and Impingers (Container No. 2). 46
    5.3.3 Contents of 4th and 5th Impingers (Container No. 3) 50
    5.3.4 Florisil® and XAD-2® Adsorbents. 50
    5.3.5 Silica Gel 51
    5.3.6 Raw Waste. 51
  5.4 Analytical Procedures and Results 52
    5.4.1 GC/HRMS. 53
    5.4.2 GC/ECD 60
    5.4.3 Ion Chromatography 62
  5.5 Quality Assurance and Quality Control 64
  5.6 Results of Analyses for TCDFs and TCDDs 68
6. DESTRUCTION EFFICIENCIES 71
7. REFERENCES 77

CONTENTS (Concluded)

APPENDICES

A Chief Engineer's Voyage Report 80
B Example Calculations 91
C Selected Portions of EPA Research Permit No. HQ-81-002 100
D Evaluation of Use of Teflon® Heat-Traced Line. 114
E Glassware Cleaning Procedure 120
F Comparison of Analytical Results from University of Nebraska (UNL) AND EMSL (EPA) 124
G EMSL, EPA Report on Quality Assurance Effort on Analysis of TCDFs AND TCDDs. 136
H University of Nebraska-Lincoln Report on Analyses of Test Samples for TCDFs AND TCDDs. 159
I Research Triangle Institute's Report on Quality Assurance Effort on the Analyses of Audit Samples for PCBs 185

FIGURES

Number Page

1 Geographical relationship of Gulf Ocean Incineration Site to nearby land masses. 2

2 M/T VULCANUS - oceanic incineration vessel 6

3 Schematic of cargo tank layout 6

4 Configuration of incinerators. 9

5 Locations of burners and thermocouples 9

6 Sampling train used during second PCB research burn. 17

7 Schematics of traps containing XAD-2® (top) and Florisil® (bottom) 19

8 Photograph of probe-beam assembly on the M/T VULCANUS. 20

9 Schematic of gas sampling probe. 21

10 Photograph of probe and port in the starboard stack. 23

11 Photograph of an assembled train 24

12 Schematic of M/T VULCANUS showing locations of wipe-samples. . 37

TABLES

Number		Page
1	Specifications of the M/T VULCANUS	7
2	Calculated Composition of the Cargo	30
3	Feed Rates of Waste During the Tests	31
4	Data from the Combustion Gas Sampling	32
5	Characterization of the Combustion Effluent	33
6	Flow Rates of Combustion Effluent	34
7	Daily Average Wall Temperatures	35
8	Results of Analyses of Wipe-Samples	41
9	Sample Work-up Parameters	47
10	pH of Impinger Solutions	48
11	Gain of Water by Silica Gel Samples	51
12	Results of Proximate/Ultimate Analyses of Samples of Waste	52
13	PCB Isomers Used to Determine Response Factors	54
14	Concentration of PCBs in the Raw Waste by GC/HRMS	56
15	Concentration of Chlorobenzenes in the Raw Waste by GC/HRMS	56
16	Minimum Detection Limits of the Method for PCBs by GC/HRMS (pg/μL) and TBB Recoveries	58
17	Minimum Detection Limits of the Method for Chlorobenzene by GC/HRMS (pg/μL)	59
18	Concentration of PCBs in the Raw Waste by GC/ECD	61
19	Results of Ion Chromatographic Analyses for Chloride Ion	63
20	Concentration of PCBs in QA Samples by GC/HRMS	65
21	Concentration of PCBs in QA Samples by GC/ECD	66
22	Quality Assurance Results	67
23	Concentrations of TCDFs in the Waste	69
24	Concentrations of TCDFs in Stack Gas Samples	70

TABLES (Concluded)

Number		Page
25	Destruction Efficiencies of PCBs.	72
26	Destruction Efficiencies of Chlorobenzenes.	74
27	Destruction Efficiencies of TCDFs	76

ACKNOWLEDGEMENTS

Work on this project was started on 20 July 1982. Less than one month later, on 15 August, the M/T VULCANUS was able to sail, all of the test equipment having been installed. The successful completion of this project was the result of the cooperation and assistance of a large number of individuals and their respective organizations.

Technical direction of this project was received from a number of organizations within the Environmental Protection Agency (EPA). These included Industrial Environmental Research Laboratory (IERL), Research Triangle Park (RTP), NC, and Cincinnati, OH; Office of Water, Washington, DC; and Industrial and Extractive Processes Division, Washington, DC. In particular, the Project Officer, Mr. M. D. Jackson, Technical Support Staff, IERL/RTP, was the focal point for technical direction and assisted during the sampling activities onboard the M/T VULCANUS. Mr. Wayne Fowler of IERL/RTP assisted during the testing onboard the vessel.

Design and development of equipment, definition of test requirements, performance of the test, and analyses of the samples were performed by personnel from the Energy and Environmental and Energy Technology Divisions of TRW Inc., Redondo Beach, CA, and Research Triangle Park, NC. Analyses of the samples for tetrachlorodibenzofurans (TCDFs) and tetrachlorodibenzo-p-dioxins (TCDDs) were performed by personnel of the Chemistry Department, University of Nebraska-Lincoln (UNL), Lincoln, NE, and the Environmental Monitoring Systems Laboratory (EMSL)/RTP.

The management of Chemical Waste Management, Inc. (CWM), Oak Brook, IL, and Ocean Combustion Service BV (OCS), Rotterdam, The Netherlands, facilitated the necessary engineering and scheduling liaison. The officers and crew of the M/T VULCANUS provided considerable assistance in installing and removing the test equipment.

The authors are indebted to the many individuals of all of the above organizations for their contributions to the performance of this project. In particular, the authors express their gratitude to Dr. R. A. Venezia, TRW Task Manager, and Mr. W. F. Wright who had hands-on responsibility for preparing for and performing the testing.

1. INTRODUCTION AND SUMMARY

1.1 INTRODUCTION

Thermal destruction of combustible wastes at sea is recognized as an alternative to land-based incineration. In August of 1974 (1), March of 1977 (2), and July-September 1977 (3,4), testing sponsored by the U.S. Environmental Protection Agency (EPA) was performed while the M/T VULCANUS was burning organochlorine wastes. Results of these tests were evaluated by EPA, and it was concluded that oceanic incineration was an environmentally acceptable and cost-effective alternative to other means of disposal (5-8).

The first at-sea incineration of wastes containing polychlorinated biphenyls (PCBs) was performed in U.S. waters under EPA permit HQ-81-002 (9) during the period December 1981 - January 1982. The wastes were burned on the incinerator ship M/T VULCANUS which is operated by Ocean Combustion Service (OCS) BV, Rotterdam, The Netherlands. The wastes were supplied by Chemical Waste Management (CWM), Inc., Oak Brook, IL from its facility in Emelle, AL. CWM and OCS were the permittees. OCS is a wholly owned subsidiary of CWM. An extensive sampling, monitoring, and analysis project was performed during the first burn and has been reported in detail (10,11).

During the period 15-31 August 1982, a second shipload of PCB-containing wastes supplied by CWM was incinerated by the M/T VULCANUS also under research permit HQ-81-002 which allowed up to 3.6 million gallons of wastes to be incinerated. EPA sponsored a test project during this second burn, and this document reports the results of testing to measure emissions of unburned PCBs, chlorobenzenes (CBs), tetrachlorodibenzofurans (TCDFs), and tetrachlorodibenzo-p-dioxins (TCDDs).

1.2 SUMMARY OF RESULTS

Incineration operations occurred in the Gulf Ocean Incineration Site designated by EPA for oceanic incineration and defined by the following coordinates (12):

- 27°00'00" N. lat. - 94°00'00" W. long.
- 27°00'00" N. lat. - 93°20'00" W. long.
- 26°20'00" N. lat. - 93°20'00" W. long.
- 26°20'00" N. lat. - 94°00'00" W. long.

The location of the site, shown schematically in Figure 1, is centered 315 km (196 mi) SSE of Galveston, Texas, and 350 km (217 mi) S of Cameron, Louisiana and occupies an area of about 4,900 km² (1,890 mi²).

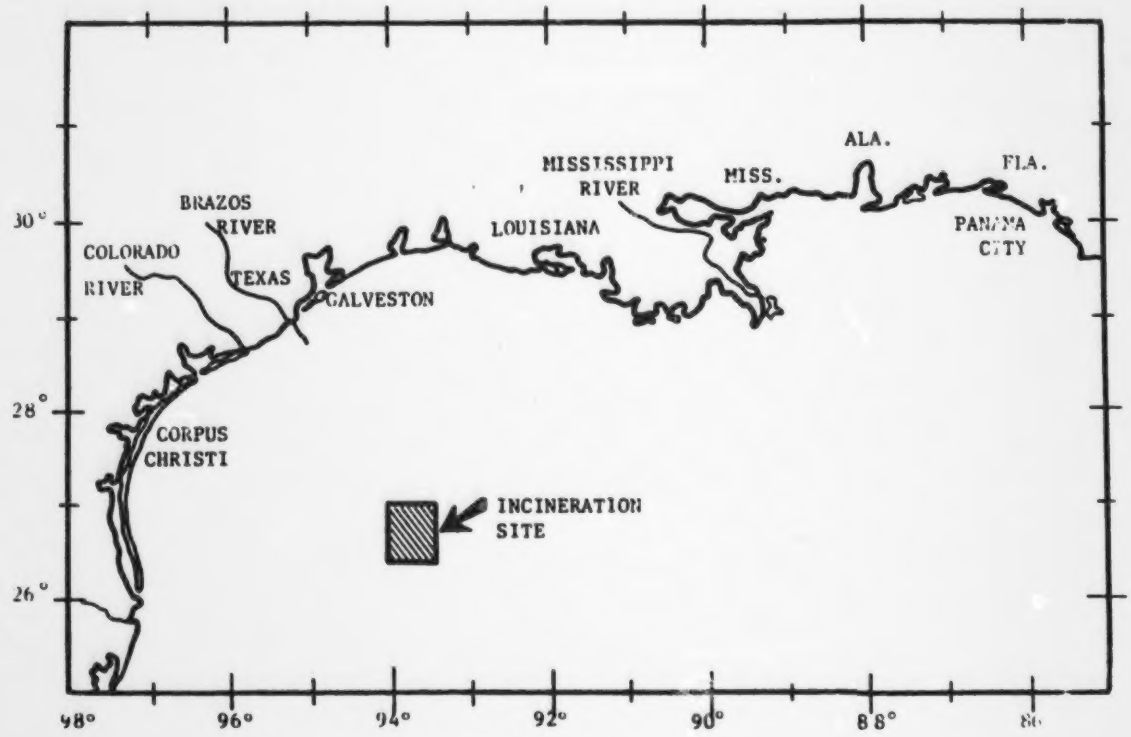

30°
28°
26°
98°
96°
94°
92°
90°
88°
COLORADO RIVER
BRAZOS RIVER
TEXAS
GALVESTON
CORPUS CHRISTI
LOUISIANA
MISSISSIPPI RIVER
MISS.
ALA.
FLA.
PANAMA CITY
INCINERATION SITE

Figure 1. Geographical relationship of Gulf Ocean Incineration Site to nearby land masses.

The M/T VULCANUS left CWM's dock in Chickasaw (Mobile), AL on 15 August 1982 (13, Appendix A). Incineration operations started on 17 August and were completed on 29 August. The vessel returned to dock at Chickasaw on 31 August. The cargo was 3,523 metric tons (mt) (3,883 tons) in weight and 3,031 cubic meters (m^3) (801,000 gallons) in volume (Appendix B.1). Incineration operations required 282 hours, and a total of 3,507 mt was destroyed.

Ten tests were performed. (A test consisted of the acquisition of a sample of stack gas and a sample of waste, time-composited over the stack sampling period.) Combustion gases were sampled with a train mandated for use in testing land-based incinerators for emissions of PCBs (14). It is essentially an EPA Method 5 (15) train, modified to incorporate an adsorbent-filled tube to trap PCBs and other specified organic compounds emitted in the stack gas. Air in the dining and incineration control rooms was sampled to determine if PCBs were present. Selected areas of deck surface were sampled with filter paper for contamination, and these samples were analyzed onboard to determine compliance with the health and safety plan. Samples of the waste and process-related data, such as wall temperatures and concentrations of CO, CO_2, and O_2 in the combustion gases, were acquired from the Chief Engineer.

Averages of measured process-related incineration parameters were:

- Waste feed rate: 12.43 mt/hr, 10.7 m^3/hr (total)
- Wall temperature: 1303°C
- Concentration of O_2: 10.1%
- Concentration of CO_2: 9.1%
- Concentration of CO: 8 parts per million (ppm)
- Excess air: 95%
- Residence time: 1.3 sec

The personnel protection procedures described in Chapter 4 worked satisfactorily. The boundary-isolation concept developed for the at-sea incineration of Herbicide Orange (3) was again employed and was effective in preventing the spread of cargo into living areas of the ship.

Results of the analyses of the stack gas samples and of the process-related data demonstrate that the performance of the incineration process, as measured by destruction and combustion efficiency, was consistently greater than the required 99.9 percent (9).

The remainder of this report is organized as follows: Chapter 2 describes the M/T VULCANUS, Chapter 3 describes the testing, Chapter 4 presents results of the test operations, Chapter 5 gives results of the analyses, and Chapter 6 presents destruction efficiencies. There are nine appendices: A, voyage report of the Chief Engineer; B, example calculations; C, selected portions of research permit HQ-81-002; D, evaluation of a heat-traced Teflon® line; E, procedures for cleaning glassware; F, EPA summary report of analyses of TCDFs and TCDDs; G, EPA report on the quality assurance effort on the analyses of TCDFs and TCDDs; H, University of Nebraska-Lincoln report on the analyses of test samples for TCDFs and TCDDs; and I, Research Triangle Institute report on the quality assurance effort on the analyses of audit samples for PCBs.

2. DESCRIPTION OF THE M/T VULCANUS

2.1 GENERAL LAYOUT OF THE VESSEL

The M/T VULCANUS, originally a cargo ship, was converted in 1972 to a chemical tanker fitted with two large liquid injection incinerators located at the stern. The M/T VULCANUS is a double-hull, double-bottom vessel which meets all applicable requirements of the International Maritime Organization (IMO)* concerning transport of dangerous cargo by tanker. Figure 2 is a picture of the vessel, and Table 1 gives some of the ship's specifications. Both the picture and the table were furnished by Ocean Combustion Services BV, Rotterdam, The Netherlands, which operates the vessel. Because of her size - an overall length of 102 meters, a beam of 14.4 meters, and a maximum draft of 7.4 meters - the M/T VULCANUS is able to operate worldwide. Two diesel engines drive a single propeller to give cruising speeds of 10 to 13 knots. Her crew numbers 19; thirteen to operate the vessel and six to operate the incinerators.

2.2 TANKS AND PUMPS

Waste is carried in 15 cargo tanks ranging in size from 112 to 574 cubic meters (m^3) with an overall capacity of 3,503 m^3. Tanks 6P and 6S are no longer used for cargo, so that the vessel's typical capacity is 3,279 m^3. Figure 3 is a schematic of the cargo tank layout. Tanks are filled through a manifold on deck using a dockside loading pump. During normal operation, the waste tanks can be discharged only through the incinerator feed system. There is, however, provision for discharging the cargo into the ocean if an emergency arises. Piping is arranged so that any tank can be connected to either incinerator and cargo can be transferred between any two tanks.

---

*Formerly, Inter-Governmental Maritime Consultative Organization (IMCO).

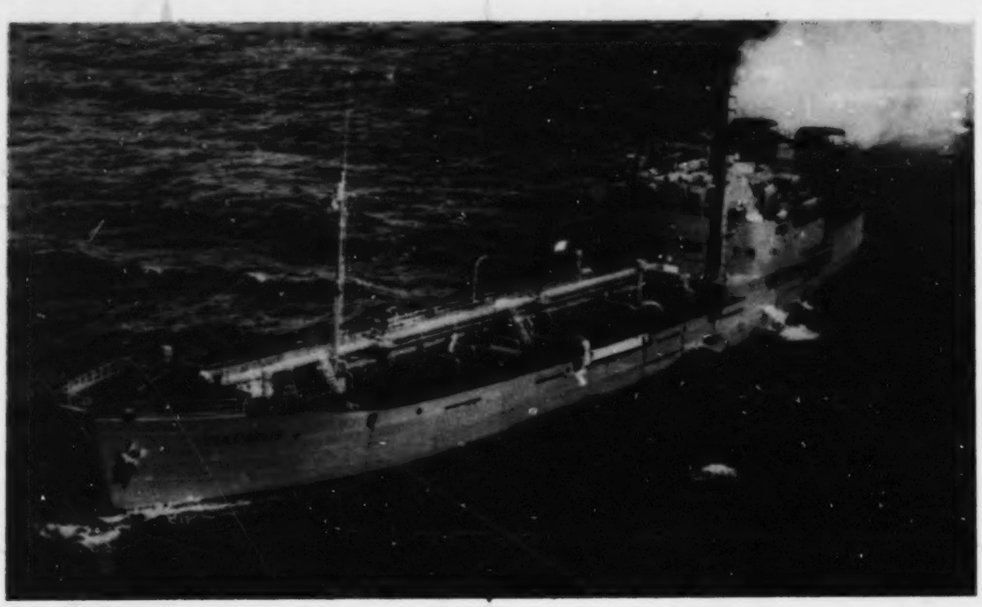


Figure 2. M/T VULCANUS - oceanic incineration vessel.

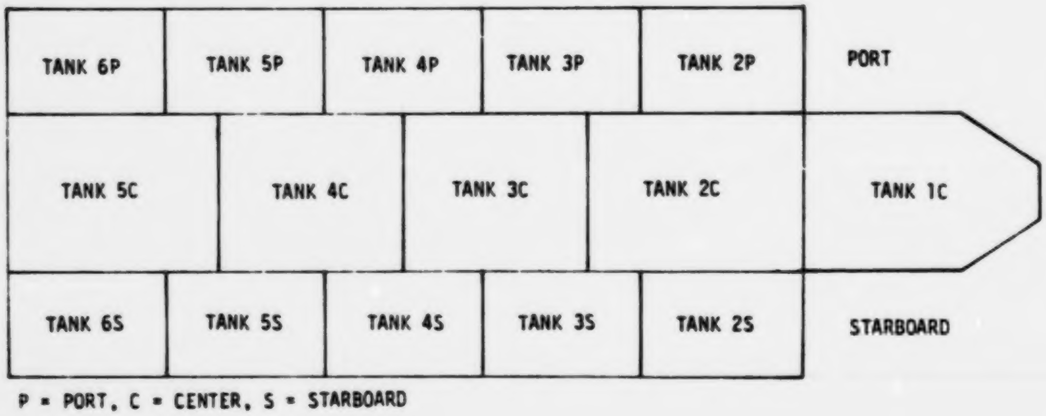

TANK 6P
TANK 5P
TANK 4P
TANK 3P
TANK 2P
PORT
TANK 5C
TANK 4C
TANK 3C
TANK 2C
TANK 1C
TANK 6S
TANK 5S
TANK 4S
TANK 3S
TANK 2S
STARBOARD
P = PORT, C = CENTER, S = STARBOARD

Figure 3. Schematic of cargo tank layout.

TABLE 1. SPECIFICATIONS OF THE M/T VULCANUS

Length overall	101.95 meters
Breadth	14.40 meters
Draft, maximum	7.40 meters
Deadweight (DWT)	4,768 metric tons
Speed	10-13 knots
Tank capacity	3,503 cubic meters (cu m)
Number of tanks	15, ranging in size from 115 cu m to 574 cu m
Tank coating	No coating in tanks, pipes, pumps, etc. All equipment consists of low carbon steel
Loading equipment	Not available, but can be placed on board, if required
Hose connection	10.2, 15.2, and 20.3 centimeters (4,6, 8 inches)in diameter
Safety equipment	Specially designed for this task and in accordance with latest regulations of IMCO, Scheepvaart-Inspectie (The Hague)
Waste to be processed	Must be liquid and pumpable. May contain solid substances in pieces up to 5 centimeters in size. Must not attack mild steel
Incinerators	2
Per incinerator:	
Overall height	10.45 m
Combustion chamber	
OD	5.5 m
ID	4.8 m
Stack (top)	
OD	3.8 m
ID	3.4 m
Waste feed (max)	12.5 metric tons/hour
Combustion air (max)	90,000 m^3/hour
Burners (Vortex type)	3
Volume	120 m^3
Residence time	1.0 sec at 1500 °C (calculated)

The space between the two hulls is used for ballast. Ballast tanks are filled with seawater and emptied independently as required to trim the ship. Fuel oil is carried in tanks under and in the engine room. The engine room is separated from the cargo tanks by double bulkheads. The pump room and generator room are situated between the engine room and the waste tanks.

2.3 INCINERATION SYSTEM

Waste is burned in two identical, refractory-lined furnaces located at the stern. Each incinerator consists of two main sections: a combustion chamber and a stack, through which the combusting gases pass sequentially as shown in Figure 4. This dual chamber configuration is characteristic of most high intensity combustion systems and uses the first chamber for combustion and the second to increase residence time and the exit velocity of the combustion gases. Each incinerator is equipped with three burners.

Combustion air is supplied by six large fixed-speed blowers, one per burner, with a rated maximum capacity of 90,000 cubic meters per hour for each incinerator. Flow is controlled by adjustable vanes which, when deflected, increase or decrease system pressure drop and reduce or increase air feed rate, respectively. During normal operation air feed rate is calculated to be between 65,000 and 75,000 cubic meters per hour at ambient conditions.

Liquid wastes are fed to the combustion system by means of electrically driven pumps. A device (Gorator) for reducing the solids in the waste to a pumpable slurry is located upstream of the metering pump for each burner. The Gorator also recirculates the waste through the waste tanks, thereby mixing their contents. Power for the blowers, pumps, and other parts of the incinerator system is supplied by two diesel-generators with a total capacity of 750 kW at 440 V and 50 Hz.

The burners are located at the same level on the periphery of each incinerator near the base. The burners are of the rotary cup type and deliver waste or fuel oil through a central tube to atomization nozzles near the periphery of the rotating cup. High velocity air delivered through an outer annulus, shapes the flame. As shown in Figure 5, the burners are directed tangentially to the vertical axes of the incinerators, thereby imparting swirl to and better mixing of the combustion gases.

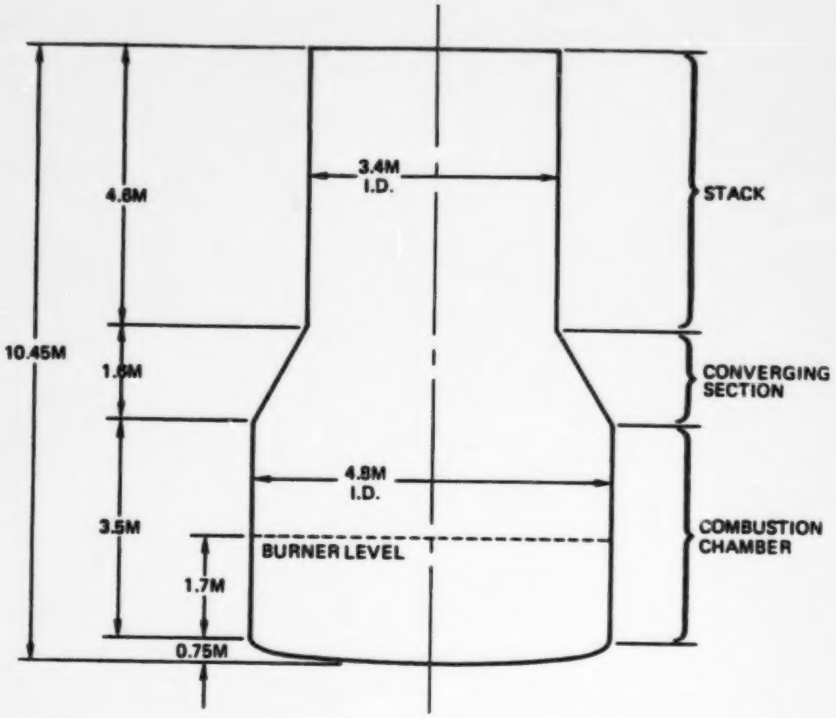

3.4M
I.D.
4.8M
STACK
10.45M
1.6M
CONVERGING
SECTION
4.8M
I.D.
3.5M
BURNER LEVEL
COMBUSTION
CHAMBER
1.7M
0.75M

Figure 4. Configuration of the incinerators.

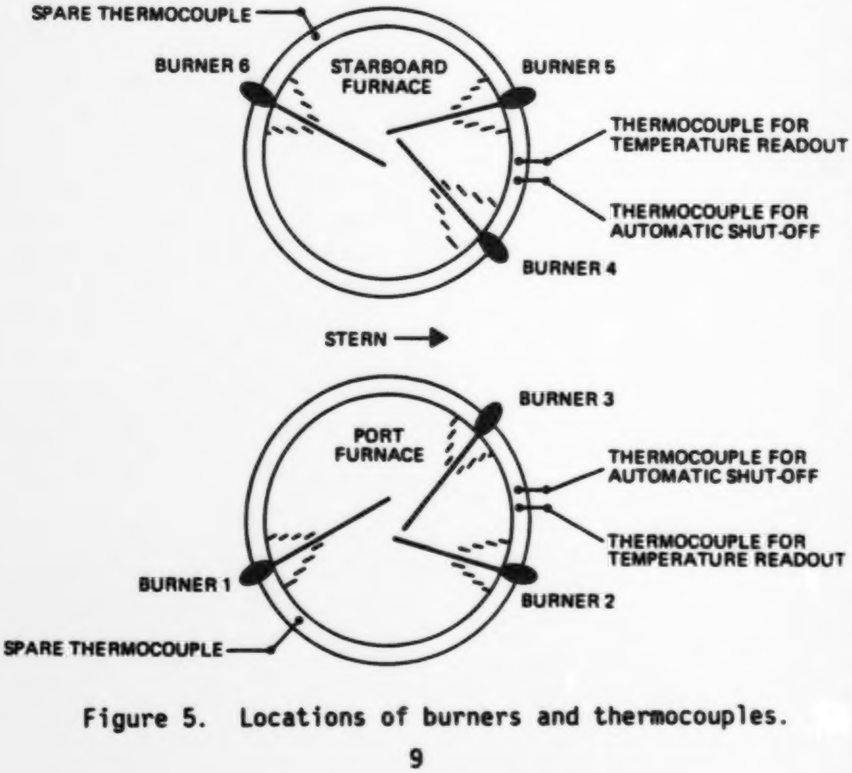

SPARE THERMOCOUPLE
BURNER 6
STARBOARD
FURNACE
BURNER 5
THERMOCOUPLE FOR
TEMPERATURE READOUT
THERMOCOUPLE FOR
AUTOMATIC SHUT-OFF
BURNER 4
STERN
BURNER 3
PORT
FURNACE
THERMOCOUPLE FOR
AUTOMATIC SHUT-OFF
THERMOCOUPLE FOR
TEMPERATURE READOUT
BURNER 1
BURNER 2
SPARE THERMOCOUPLE

Figure 5. Locations of burners and thermocouples.

A three-way valve is employed on each burner to provide a waste feed, a fuel oil feed, or a shut-off condition. Although waste and fuel oil cannot be fed into a burner simultaneously, alternate burners can be operated with fuel and waste to achieve higher or lower combustion temperatures if necessary, depending on the relative heat contents of the fuel oil and waste.

Periodically during the incineration process, the burners require cleaning. Normally, each incinerator is shut down, and the three burners are cleaned sequentially. When only a single burner needs cleaning (should flow to that one become too low), the remaining two continue to fire waste. Cleaning is easily accomplished, and the normal period required to clean three burners is less than one-half hour. After cleaning, burners are re-started on fuel oil until minimum operating temperature is reached. Burners are then switched sequentially to waste. Carbonized material resulting from cleaning the burners is burned in the incinerators.

2.4 MEASUREMENT OF WASTE FLOW RATE

Sounding the depth of waste in each tank over time with a tape is the method of determining burn rate. The accuracy of this method is best in port or in calm seas (i.e., minimum motion). During operations, the total time is recorded for emptying each tank, and a time-averaged waste feed rate is determined.

Recent EPA permits (9) have required that, when a tank is near depletion, two burners per incinerator be switched to a fresh, full tank and that feed from the tank near depletion be continued through the one remaining burner per incinerator until the tank is empty. This procedure is intended to eliminate flame-outs. It is planned to upgrade the closed gauging system for measuring waste feed rate while the vessel is undergoing major modifications (personal communication, D. G. Ackerman with G. Heinemann, Director of OCS, November 1982).

2.5 THERMAL MEASUREMENTS

In 1980, the temperature measurement system was changed. Currently, there are three wall thermocouples (platinum-platinum/10% rhodium) at the burner level (Figure 5) in each incinerator. Two of these serve the automatic waste shutoff system: one is the primary, and the other is a spare which can be connected by changing the position of a switch if the primary fails. The signal from the spare is also supplied to the temperature readout system by the switch. The third wall thermocouple in each incinerator supplies the primary signal to the temperature readout system. The primary thermocouples for the temperature readout and automatic waste shut-off systems are located about 20 cm apart between burners 2 and 3 and burners 4 and 5, respectively. The spare thermocouples are placed between burners 1 and 2 and between burners 5 and 6, respectively. As in the past, there is a thermocouple placed in about the middle of the tapered portion of each stack. This is the "outlet" thermocouple, and its signal is connected to the temperature readout system. All four thermocouples are placed flush with the inner wall. Flame temperatures were previously determined to be 250 to 300°C higher than those indicated by the wall thermocouples (2).

Before 1980, temperatures during operation of the incinerators were measured by a pair of platinum-platinum/10% rhodium thermocouples in each incinerator. Each pair was located in wells between burners 2 and 3 and burners 4 and 5. One thermocouple was located approximately 1.3 cm from the inside surface of the refractory lining, served the automatic waste shut-off system, and was called the controller thermocouple. The second thermocouple, approximately 4 cm from the inner surface of the firebrick, was referred to as the indicator thermocouple because it provided temperature information to a panel located in the incinerator control room and to the panel being photographed for the record in a sealed "black box" (see Section 2.3) located on the bridge (2).

2.6 EMERGENCY AUTOMATIC WASTE SHUTOFF

The waste shutoff system consists of a number of different components which can effect the closing of spring-loaded solenoid valves which shut off flow of waste to each burner and the simultaneous termination of power to the waste metering pumps. During incineration, waste flows through the solenoid valves unless the electrical current holding the valves open is interrupted by a malfunction in the incineration system. (These spring-loaded solenoid valves are normally closed.) Once interrupted, the malfunction must be repaired and restart procedures implemented before incineration can continue.

These restart procedures require fuel oil start-up if the incinerator temperature has dropped below a specified minimum temperature.

The automatic waste shutoff system will stop waste flow (or fuel oil flow) to the affected burner(s) and shut off power to the waste metering pumps when any one of the following events occur:

- Overload of a Gorater
- Overload of a combustion air fan motor
- Overload of a burner metering pump
- Failure of steering air (directs and shapes burner flame) or combustion air to reach burner
- Open burner (e.g., burner swung away from mount for cleaning)
- Loss of flame
- Reduction in temperature below a set-point

Once flow has been stopped by the automatic shutoff system and any malfunctions are repaired, the following restart procedures are implemented:

- Waste pumps (or fuel oil pumps if incinerator temperatures are low enough to require fuel oil startup) are manually restarted.
- Ignitor buttons on the burners are pushed to provide ignition flame. Burners are ignited sequentially.
- The emergency shutoff valve on each burner is opened manually to initiate waste (or fuel oil) flow.
- After stable combustion is attained, manual override of the emergency shutoff valves is deactivated, returning the system to automatic shutoff control.

A major regulated control parameter is wall temperature. If wall temperatures fall below a pre-set minimum value, a Plastomatic 2000® system on each incinerator shuts off flow of waste and metering pumps. The temperature-set dials on the Plastomatics® are mounted in cases which provide visibility but which can be (and are) sealed by cognizant government officials. The usual set-point of the Plastomatics® is 1250°C, which is above the minimum of 1200°C required by international regulations in order to minimize unnecessary shut-downs caused by small, normal fluctuations in temperature resulting from normal variations in flow rate and heat content of waste feed.

Before starting the burn, another contractor to EPA performed a quality assurance (QA) audit of the thermal measurement system. The wall thermocouples gave acceptable results. However, the starboard Plastomatic® dial was found to be 65°C too low. That is, at an indicated setting of 1200°C, the wall temperature would actually be 1265°C. Consequently, at the usual indicated setting of 1250°C, the wall temperature would actually be 1315°C, for above either the required minimum of 1200°C or the usual setting of 1250°C. At the Chief Engineer's request, the EPA-observer lowered the set-points of the Plastomatics® so that they would shut off the flow of waste if wall temperatures fell below 1220°C and re-sealed the cases (see Appendix A).

2.7 COMBUSTION GAS MONITORING SYSTEM

In 1980, in accordance with international regulations, a system continuously monitoring concentrations of CO_2, O_2, and CO in the combustion gas was installed. Two ports for probes were installed in each incinerator. A heavy duty ceramic probe is placed in one port in each incinerator and extends about 20 cm past the inner wall. The second port is left empty, but a new probe can be installed even when the incinerators are firing wastes. Unheated Teflon® lines (approximately 6-mm O.D., 1/4-inch) connect the probes to the monitoring system. These lines (two per incinerator) are routed through thin-walled metal tubing for protection. The tubing is run downhill; there are no low points.

The gas conduit lines enter the bridge where the monitoring system is installed. The system was designed and installed by Siemens, AG, Federal Republic of Germany. Components of the system are: water-filled gas bubblers to remove acidic gases and particulate matter, refrigeration-based gas conditioners to cool the gas and remove moisture, filters to complete the removal of particulate matter, monitors, pumps, electronics, and calibration gases. Specifications of the monitors are:

- CO_2 - Ultramat 1, Model M52009, non-dispersive infrared, 0-20% (v/v)
- CO - Ultramat 2, Model M52014, non-dispersive infrared, 0-500 ppm (v/v)
- O_2 - Oxymat 2, Model M52010, paramagnetism, 0-15% (v/v)

The gas stream from each incinerator is presented alternately to the combustion gas monitoring system every 15 minutes. Readouts from the monitors are located in the black box and in the control panel in the incinerator room. The system functions largely unattended except for a) daily calibrations, b) daily refilling of the gas bubblers, and c) occasional replacement of the filters.

A QA audit of the combustion gas monitoring system was also made (17). The CO_2 and O_2 monitors responded satisfactorily, but there was a problem with the CO monitor. When the span was set with ship's calibration gas (15% O_2, 10% CO_2, and 48 ppm CO) to the certified concentration of 48 ppm, the monitor gave a low reading for the audit-CO calibration gas. The audit-CO gas was checked and found accurate, and it was theorized that the ship's calibration gas had deteriorated from a concentration of 48 ppm to 33.6 ppm of CO. The EPA-observer thus directed the ship's electrician to set the span of the CO monitor to 33.6 ppm rather than 48 ppm.

After returning to port, it was determined that the problem was one of spectral interference, and that the ship's calibration gas had not deteriorated. As noted above, the ship's calibration gas contained 10% CO_2, whereas the audit-gas did not. In spite of a very high degree of selectivity for CO over CO_2, the CO monitor does in fact respond slightly to CO_2. Thus, a monitor set to 48 ppm with a mixture of 48 ppm CO and 10% CO_2, would not read the same if a gas containing 48 ppm CO but no CO_2 were admitted. In this case, 10% CO_2 gives a reading corresponding to 14.4 ppm of CO. Having set the span to 33.6 ppm rather than 48 ppm, however, compensated for the response to CO_2.

Certain equipment has been installed on the M/T VULCANUS because of its particular type of operation. These items include:

- Natigational Systems: The primary navigational device is a computerized satellite-based system. A secondary system is a Decca unit for European waters. Equipment and tables for celestial navigation are also present onboard.
- Anemometer: This equipment measures the velocity and force of the wind. It is, therefore, useful in selecting an attitude of the ship during various wind conditions so that the plume may be directed away from the ship and its personnel.

- Radio Communication: The M/T VULCANUS is equipped with SSB (single side band) and DSB (double side band) radio for voice and continuous wave communication; MF (medium frequency) and SF (short wave) telegraphy; and Marifoon (VHF) (all channels) for close-in voice communication. A radio is also located on the bridge so that the watch officer can hear marine broadcasts at all times.

- Black Box: On the bridge is a panel in which is displayed the following information: wall and outlet temperatures of each incinerator; concentrations of O_2, CO_2, and CO in the stack gas and in which incinerator measurements are being made; day, date, and time; settings of the Plastomatics; status (on/off) of the metering pumps; and position (in European waters) where the Decca Navigator can receive the proper land-based signals. An automatic 35-mm camera is placed within the black box and photographs the displays every 11 minutes. Because either the black box and/or the camera can be sealed, cognizant government officials can obtain the film at the end of each voyage in order to determine whether operations were in accordance with conditions of the permit for the burn. (The camera was sealed by the EPA-observer during this burn.)

3. TEST OPERATIONS

Sampling and analytical activities were conducted in accordance with a plan (16) approved by EPA. Activities performed onboard the M/T VULCANUS were as follows:

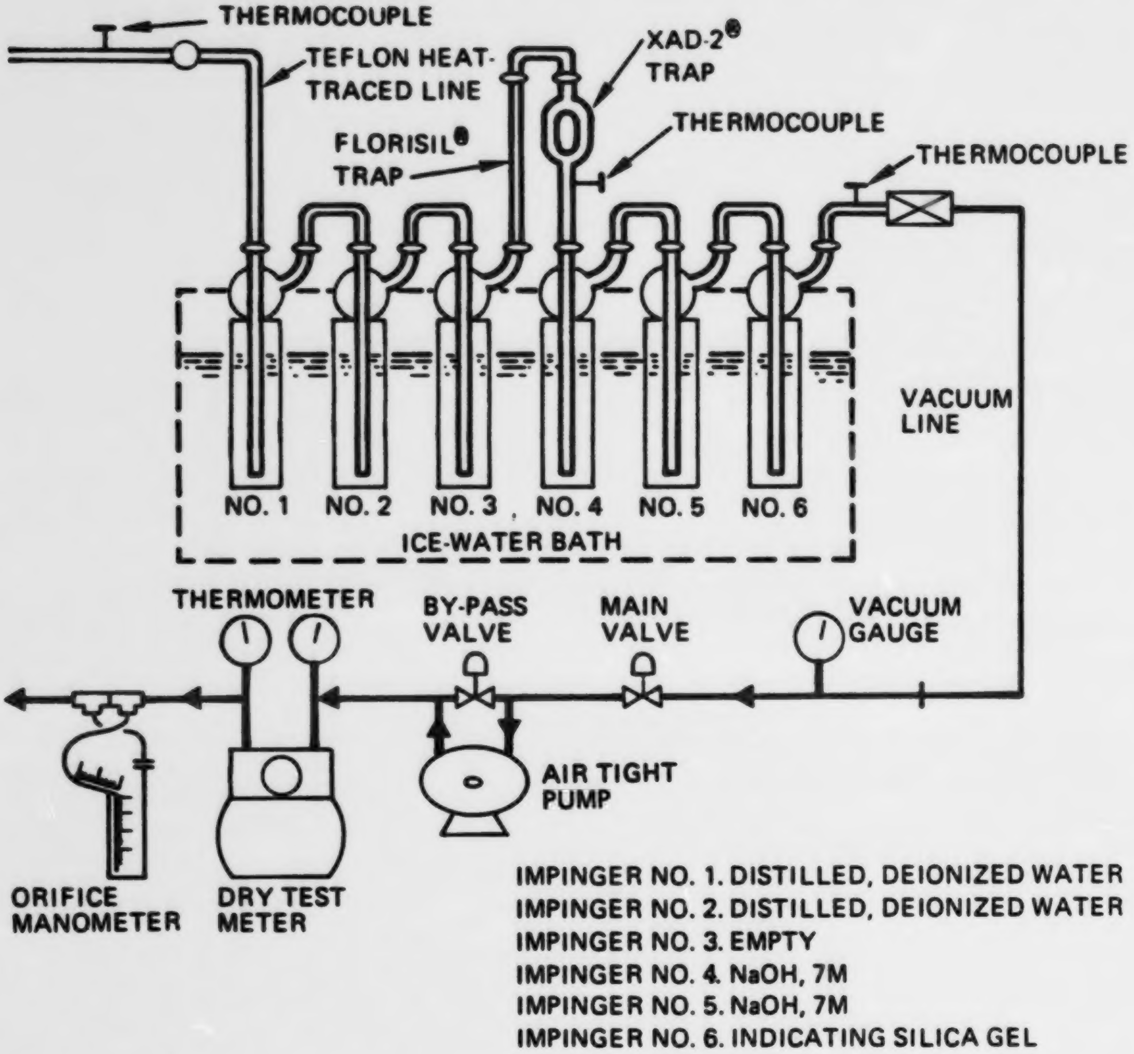
- Sampling of the stack gas
- Wipe-sampling
- Sampling of work space air
- Acquisition and reduction of process-related data

These activities are described in this chapter. Appendix C presents portions of the EPA research permit which established test requirements.

3.1 SAMPLING OF THE STACK GAS

3.1.1 Equipment

Stack gases were sampled by using the train developed (18) and mandated (14) for use during Trial Burns of PCBs in land-based incinerators. The train, a modified EPA Method 5 (15), is shown schematically in Figure 6 and consisted of the following components: two water-filled impingers, one empty impinger, an adsorbent trap filled with activated Florisil®, an adsorbent trap filled with XAD-2® resin, two impingers filled with sodium hydroxide solution, an impinger filled with activated indicating silica gel, and a meter box (pump, dry gas meter, and controls, Research Appliance Company, Gibsonia, PA). All six impingers were of Greenburg-Smith design, and all six were modified by removing the impactor tips. Leak-free seals were effected without the use of stopcock grease. Water used to fill the first two impingers was "Distilled-in-Glass" grade (Burdick and Jackson Laboratories, Muskegon, MI). Neither a cyclone nor a filter was employed because it was not necessary to acquire samples of particulate matter.


THERMOCOUPLE
TEFLON HEAT-TRACED LINE
XAD-2® TRAP
THERMOCOUPLE
FLORISIL® TRAP
THERMOCOUPLE
VACUUM LINE
NO. 1
NO. 2
NO. 3
NO. 4
NO. 5
NO. 6
ICE-WATER BATH
THERMOMETER
BY-PASS VALVE
MAIN VALVE
VACUUM GAUGE
AIR TIGHT PUMP
ORIFICE MANOMETER
DRY TEST METER

IMPINGER NO. 1. DISTILLED, DEIONIZED WATER
IMPINGER NO. 2. DISTILLED, DEIONIZED WATER
IMPINGER NO. 3. EMPTY
IMPINGER NO. 4. NaOH, 7M
IMPINGER NO. 5. NaOH, 7M
IMPINGER NO. 6. INDICATING SILICA GEL

Figure 6. Sampling train used during second PCB research burn.

The first (Florisil®) and second (XAD-2®) traps are shown schematically in Figure 7. Exclusive of connectors, the tube for Florisil® was about 10 cm long and had a 2.2 cm I.D. The contents were held in place by glass wool plugs, and the outlet end of the tube had indentations to help retain the glass wool plug. Connectors were ground glass ball (outlet) and socket (inlet) joints (§ 28/12). The tube for XAD-2® was about 10 cm long and had a 4 cm I.D. A coarse, fritted glass disc at the outlet retained the XAD-2®, and a plug of glass wool was used at the inlet. The resin bed was surrounded by a water-jacket preceded by a condenser coil. During testing, water from the ice-water bath was circulated through the jacket to maintain the temperature of the gas at the outlet of the trap at less than 20°C (68°F). Connectors were ground glass ball (outlet) and socket (inlet). When not installed in the train, the traps were sealed by being clamped to mating ball or sockets, the tube ends of which had been drawn and closed. Both the Florisil® and the XAD-2® were cleaned in accordance with EPA-approved protocols (18,19).

A 7.3 m (24 ft) long probe mounting beam was constructed by welding together two uni-strut beams [perforated steel tubes of square cross-section, 6.3 cm (2.5 in) on a side]. One end of the beam was bolted to a short I-beam used in past tests (2,3) which in turn was bolted to the flange around the sampling port. The other end of the probe mounting beam was supported by an "A"-frame made of steel tube and also used in past tests (2,3). Guy wires were attached to the beam in four places and tightened in order to minimize lateral motion of the beam.

Figure 8 is a photograph which shows the probe mounting beam, the probe (inserted into the stack), "A"-frame, and the short I-beam. Figure 8 also shows the wooden platform built by CWM for mounting the sampling train and cleaning the probe and the heat-shield, also built by personnel from CWM, to protect the sampling team from heat radiating from the incinerators.

The probe through which stack gas was drawn was the same used in several earlier tests on the M/T VULCANUS (2,3). Shown schematically in Figure 9, the probe was stainless steel-jacketed and water-cooled. The inner quartz liner extended slightly past the retaining nut at the inlet so that gas samples contacted only the quartz liner. Aspirated sample was rapidly cooled in order

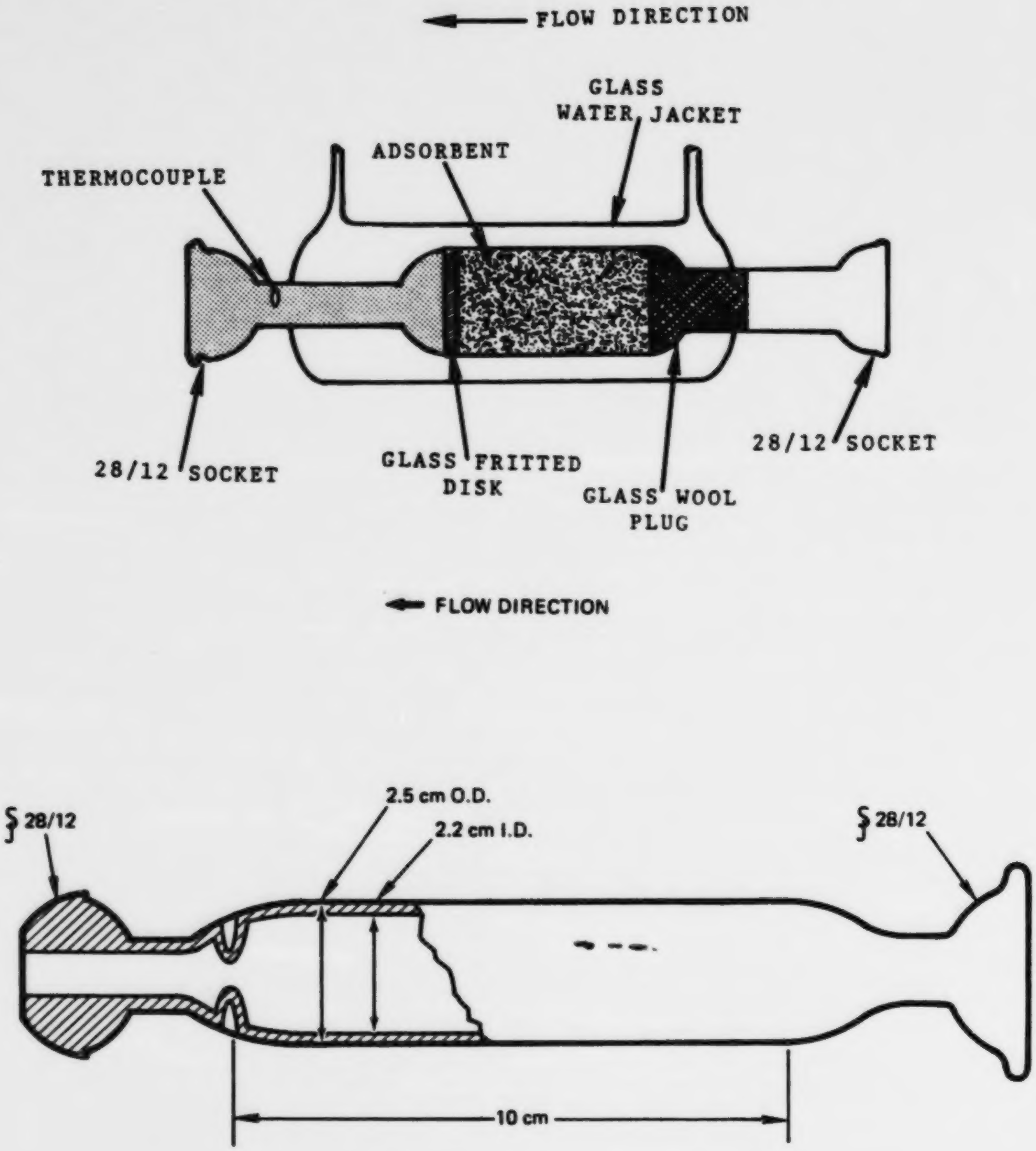

FLOW DIRECTION
GLASS WATER JACKET
ADSORBENT
THERMOCOUPLE
28/12 SOCKET
GLASS FRITTED DISK
GLASS WOOL PLUG
28/12 SOCKET
FLOW DIRECTION
§ 28/12
2.5 cm O.D.
2.2 cm I.D.
§ 28/12
10 cm

Figure 7. Schematics of traps containing XAD-2® (top) and Florisil® (bottom).

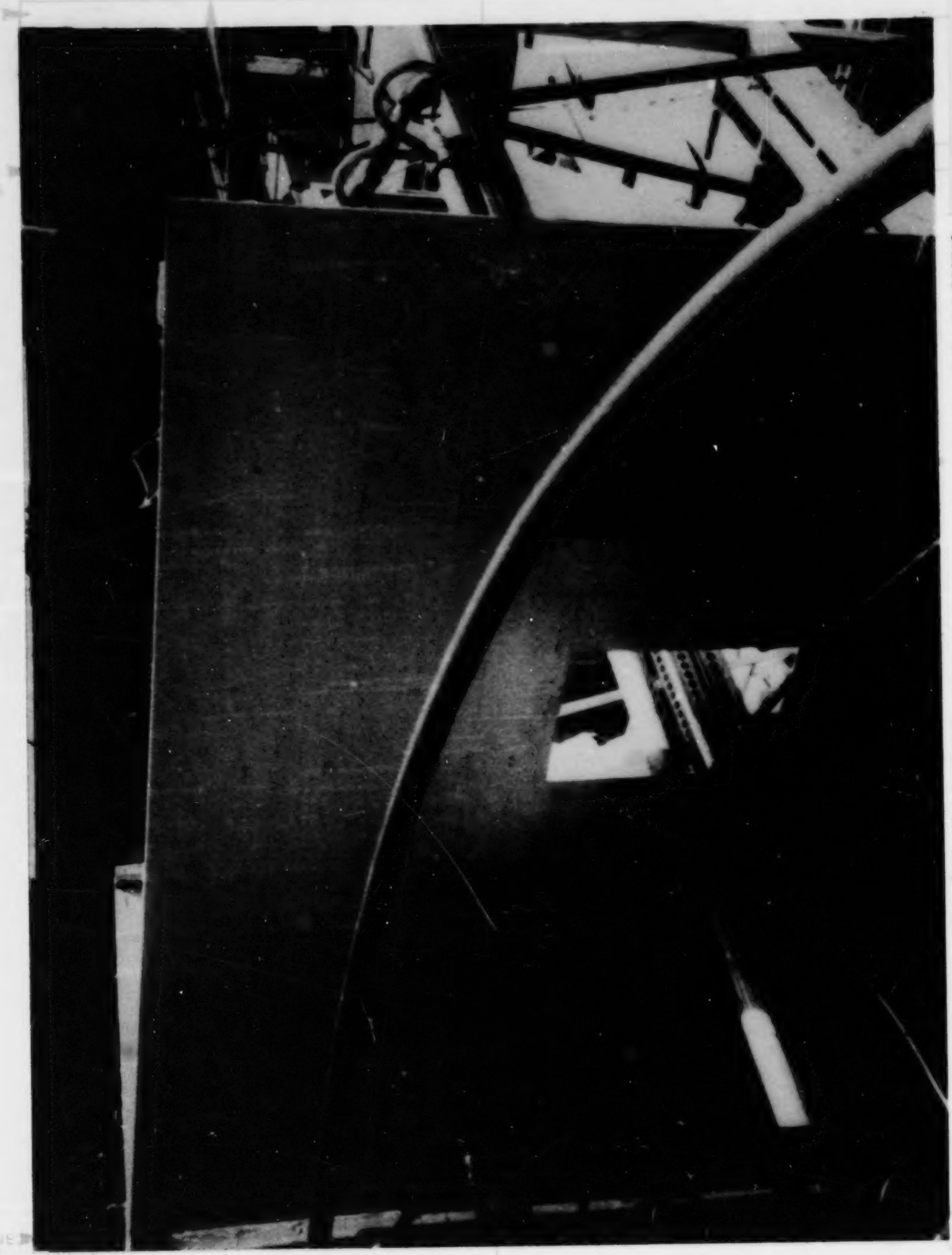


Figure 8. Photograph of probe-beam assembly on the M/T VULCANUS.

EPA Form 2350-4 (4-80)
(PREVIOUSLY CIN. EPA FORM 261)

TYPING GUIDE SHEET

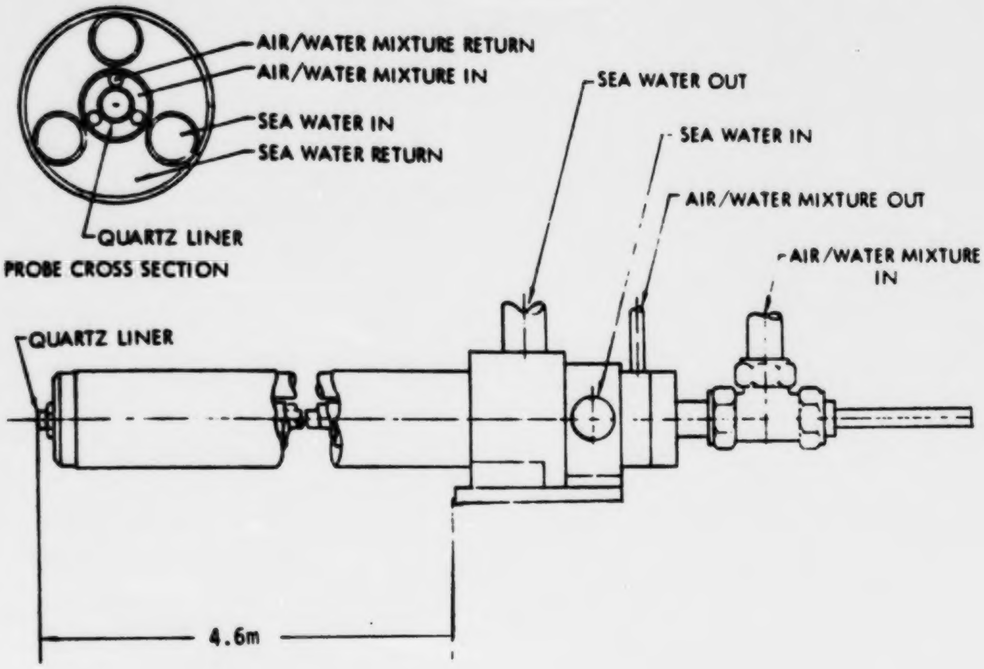

AIR/WATER MIXTURE RETURN
AIR/WATER MIXTURE IN
SEA WATER IN
SEA WATER RETURN
QUARTZ LINER
PROBE CROSS SECTION
SEA WATER OUT
SEA WATER IN
AIR/WATER MIXTURE OUT
AIR/WATER MIXTURE IN
QUARTZ LINER
4.6m

Figure 9. Schematic of gas sampling probe.

to quench further reactions in the gas. Secondary cooling by an air-water mixture was not necessary. Sampling was conducted at a fixed point and at an insertion depth of 1 meter past the inner wall of the starboard stack. At all other times, the probe was fully retracted. The probe was manually inserted and retracted.

A Teflon® tube connected the probe to the inlet of the first impinger. The tube was 1.5 m (5 ft) long, 1.3 cm (1/2 in) I.D., and 0.2 cm (1/16 in) thick wall. To minimize deposition of organic compounds, it was wrapped in heating tape, which was wrapped with waterproof insulation, and maintained at about 113°C (235°F). An evaluation of this line is presented in Appendix D.

Figure 10 is a photograph showing the probe inserted into the sampling port on the starboard incinerator. Figure 11 is a photograph showing an assembled train placed on the sampling platform. A Variac® was used to control the temperature of the heat-traced line, which is the white spirally wrapped tube connected to the inlet of the train. The heavy hoses visible carried seawater-coolant to and from the probe.

Electrical power onboard the M/T VULCANUS is standard European: 440V, 50Hz. To provide power for the sampling gear, analytical instruments, and air conditioners, a motor-generator (Sweinhart Electric Co., Inc., Los Angeles, CA) was rented and installed for the test. The ship's power operated the motor which, in turn, drove the generator, thereby converting 220V, 50Hz power to 37kVA at 220V and 60Hz.

3.1.2 Operations and Procedures

Sampling operations were generally in accordance with EPA Method 5 procedures (15), except for traversing and isokinetic sampling rate.* The nominal flow rate was 17 Lpm (0.6 cfm), and meter box+ vacuum was adjusted to maintain constant flow rates. The probe was leak-checked before installation. (Six identical probes were taken onboard, but only one was used.) No leakage of coolant water into the sample line was observed. The sampling train was leak-checked before and after each test by plugging the inlet to the heat-traced line and pulling a vacuum on the system. Leakage in excess of 0.51 Lpm (0.02 cfm or 3 percent of the nominal sampling rate) at the vacuum of 380 mm (12 in) of Hg was unacceptable.

---

*Because stack gas exits at temperatures in excess of 1200°C (2190°F), any organic compounds present in the effluent will be in the gas phase rather than being adsorbed on particulate matter. Consequently, the sampling rate did not have to be isokinetic, and traversing the stack while sampling was not required. (Ref. 3)

+Before departure from port, a QA audit was made on one of the sampling train meter boxes. The QA-contractor attached a calibrated dry gas meter to the outlet of the meter box and took five sets of data. The corrected, standard volumes of gas sampled were within the acceptable range. Pre-test and post-test calibrations of the meter boxes were made by TRW and were within the acceptable range.

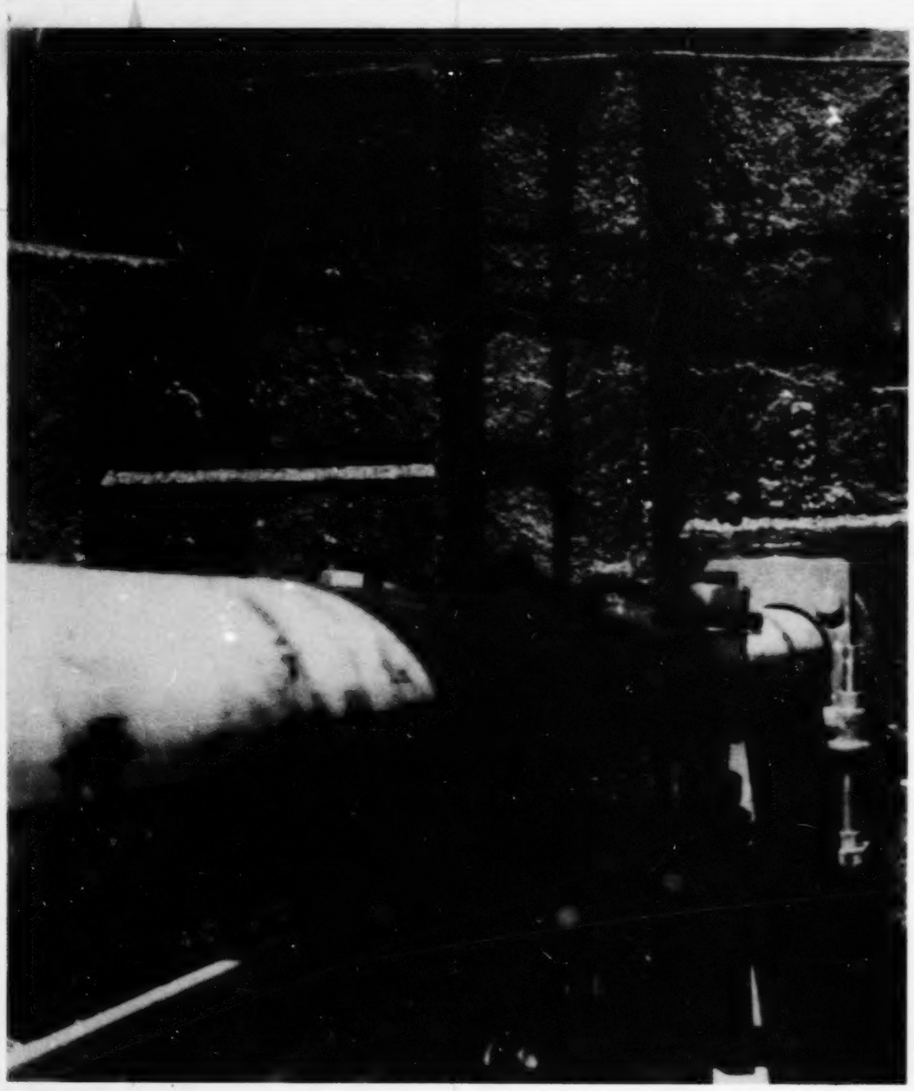


Figure 10. Photograph of probe and port in the starboard stack.

EPA Form 2350-4 (1-80)
(PREVIOUSLY CIN. EPA FORM 287)

TYPING GUIDE SHEET

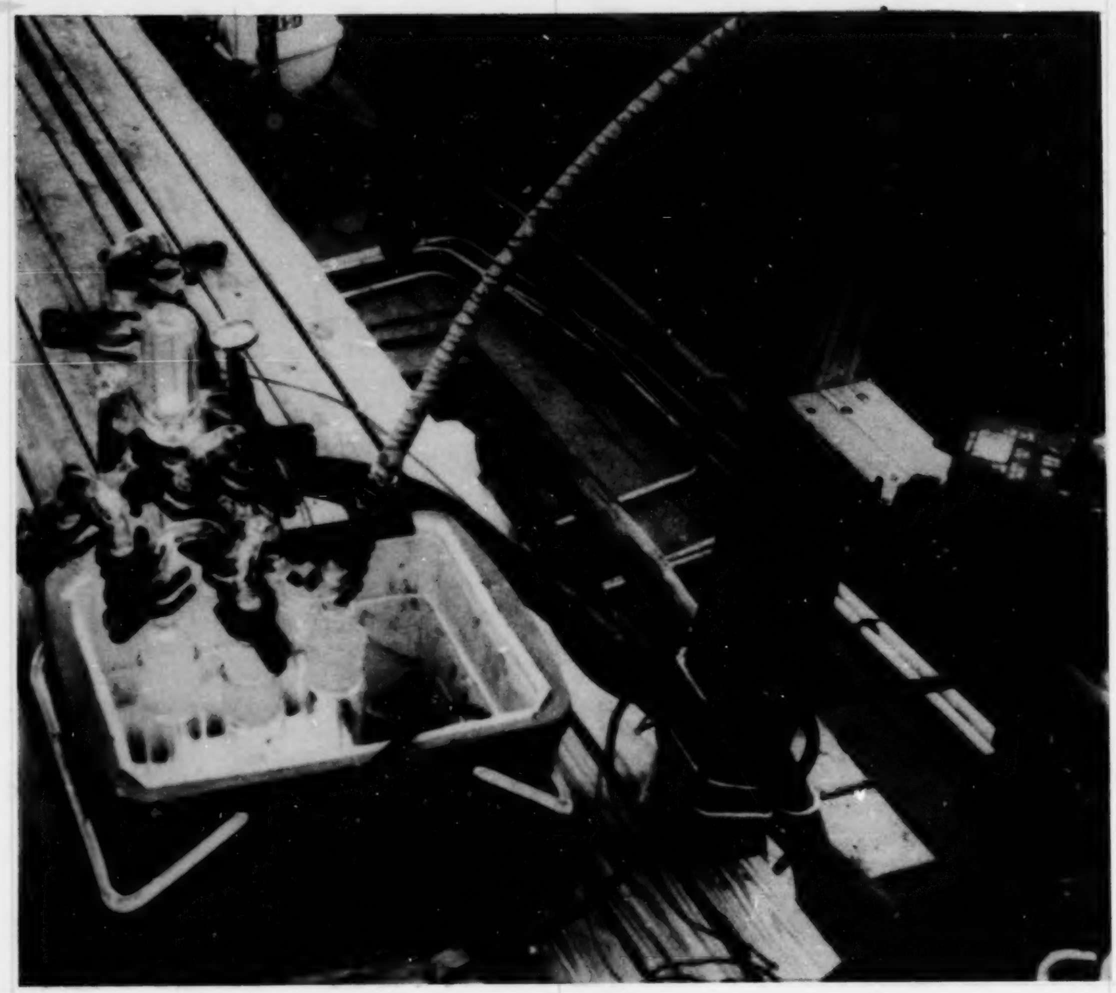


Figure 11. Photograph of an assembled train.

EPA Form 2300-4 (4-80)

TYPING GUIDE SHEET

During tests 1,5, and 10, sampling train blanks were prepared. A test consisted of the acquisition of a sample of stack gas and a sample of waste, time-composited over the stack sampling period. These trains were set up in a manner identical to the trains used in the tests except that gas was not pumped through them and were not connected to a probe. They were set in place in the vicinity of the train used for sampling for the duration of the test and were recovered in the same way as the train used in the test.

It was initially planned to perform one test per day up to a total of 10 tests. Tests 1 and 2 were performed on the first and second days of incineration. However, the ice supply was depleted more rapidly than planned because the freezer provided for this purpose did not have adequate capacity to maintain the ice supply when ambient temperatures were in excess of 38°C (100°F). (Ice was required to cool the impingers and sorbent trap containing XAD-2®.) Two tests per day were performed thereafter.

During the first test, the two impingers following the second trap were filled with 7 M NaOH to prevent hydrochloric acid (HCl) from entering the meter box. This concentration proved too great because the impingers became plugged after about 0.5 hours of sampling by precipitated Na_2CO_3. For the second test, the concentration of base was reduced to about 0.7 M. This test, too, was stopped early because the pressure drop across the train was too high. Some precipitated Na_2CO_3 was present; therefore, base was not used in subsequent tests. A single water-filled impinger replaced the two base-filled impingers during the third test; however, HCl broke through, and thereafter two water-filled impingers were used during tests 4-10. Because of the problems mentioned above, Tests 1 and 2 were shorter (about 0.5 hour) than desired. While valid, samples from these tests were of second-level priority for analysis. Tests 3-10 were of the planned 2-hour duration.* (Six valid tests were required, Reference 9. Appendix C contains requirements of the permit relevant to sampling and analysis.)

---

*International regulations promulgated by IMO (8) require the achievement of a destruction efficiency of at least 99.9 percent. Using very conservative assumptions, it was calculated that a 2-hour sampling period would provide sufficient sample to demonstrate a destruction efficiency greater than 99.99 percent.

Recovery of samples from the trains (test and blank) were performed by the following procedure:

- Probe. Rinse sequentially with about 500 mL each of acetone and hexane (both Distilled-in-Glass grade, Burdick and Jackson Laboratories). Catch rinsate in a 2 liter amber glass bottle (Container No. 1). Cap both ends of probe with aluminum foil. For rinsing, the probe was held with the inlet higher than the outlet. As rinsing fluid was added, the probe was rotated. The probe was then ready for reuse.

- Heat-traced line. Rinse sequentially with about 30 mL each of acetone and hexane. Catch rinsate in Container No. 2. Cap both ends of heat-traced line with foil. The line was then ready for reuse.

- Adsorbent traps. Remove traps from train and cap with the ground glass caps.

- Impingers 1-3. Measure and record the volumes of the contents of each impinger and then pour contents into a 1-liter amber glass bottle (Container No. 2). Rinse each impinger three times each sequentially with about 30 mL of acetone and hexane. Swirl the impinger to coat the walls with the rinsing fluid. Pour rinsate into Container No. 1.

- Impingers 4 and 5. Measure and record the volumes of the contents of these impingers. Pour contents into a 1-liter amber glass bottle (Container No. 3). Rinse each impinger three times with about 30 mL water and add rinsate to Container No. 3.

- Silica gel. Return contents of the sixth impinger to the original container for weighing in the laboratory.

3.2 CONTAMINATION CONTROL SAMPLING

The research permit (9) required implementation of a safety plan. A key feature of the safety plan was the establishment of boundaries or interfaces between areas that were, by definition, "clean" and areas that were "contaminated". It was required that decontamination measures be performed when these boundaries were crossed. Thus, when a person entered a "contaminated" area (e.g., incinerator room), he was required to don disposable coveralls and shoe covers or a second set of shoes. When a person passed from a "contaminated" to a "clean" area, he had to discard the coveralls and shoe covers or change shoes. Members of the ship's engineering staff, who spent long periods of time in the incinerator room, showered after leaving the incinerator room and before re-entering living areas. (There is a shower off the port passageway just before the entry to the incinerator room.)

In order to determine the effectiveness of the safety plan, selected areas of deck surfaces were sampled and the samples analyzed onboard the M/T VULCANUS. "Wipe" sampling was performed by moistening a filter disc (Gelman Type A/E glass fiber filter, 142 mm diameter, binder-free, Gelman Sciences, Inc., Ann Arbor, MI) with hexane and then wiping the disc over a surface of interest (typically about 25 cm x 25 cm square). After being wiped over the surface, the exposed filter was returned to its bottle and held for analysis.

The portable laboratory used in past tests (2,3) was again employed. It was refurbished, and new laboratory benches and instruments were installed. The laboratory was mounted above another standard shipping container. Power for lighting, air conditioning, and operating the instruments was supplied by the motor-generator.

A Perkin-Elmer Model 3920 (Perkin-Elmer Corp., Norwalk, CN) gas chromatograph (GC) was the principal analytical instrument. It was equipped with an electron capture detector (^{63}Ni), and the signal from the detector was reduced and recorded by a Shimadzu Model CR1A data reduction system (Shimadzu Corp., Tokyo, Japan). The column was 1.8 m (6 ft) long, 0.6 cm (0.25 in) O.D., 1.5% SP-2250 + 1.95% SP-2401 on 100/120 mesh Supelcoport (Supelco, Inc., Bellefonte, PA). Chromatographic conditions were as follows: inlet at 300°C, oven at 195°C (isothermal), interface at 300°C, detector at 325°C, carrier gas - 5% methane in argon at 33 mL/min.

A Varian Model 6000 GC (Varian Instrument Group, Palo Alto, CA) was maintained as a backup to the Perkin-Elmer instrument. It was also equipped with an electron capture detector. A Varian Model CDS-111 integrator was available as a backup to the Shimadzu CR1A unit. It was not necessary to use the backup instruments.

Every other day, eight to ten wipe samples were taken. Upon return to the portable laboratory, a 10-mL volume of hexane was added to each sample bottle. The bottles were shaken several times every other minute for a total of 10 minutes. Extracts thus prepared were then decanted into 15-mL screw cap vials and held for analysis.

3.3 OTHER SAMPLES AND MEASUREMENTS

3.3.1 Sampling of the Waste

Manually operated valves were placed in the waste feed lines to burners Nos. 4 and 5. At the start, end, and at 30-minute intervals during a test, samples of the waste, about 150 mL in volume, were drawn from the line to burner No. 4. These samples were placed into a 1-liter amber glass bottle. Thus, samples of the wastes were actually composites made over the duration of each test. Frequently, wastes from two tanks were fed simultaneously to the incinerators. Operationally, this involved feeding waste from one tank into two burners per incinerator and waste from the second tank into one burner. In these situations, sampling of the waste was done proportionally: two 150-mL aliquots of the waste being fed to two burners and one 150-mL aliquot of the waste being fed to one burner were taken (again, at the start, end, and at half-hour intervals).

3.3.2 Sampling of Work-Space Air

In order to determine what, if any, ambient levels of PCBs existed in the work-space, samples of air were taken at two locations: the dining room and at the control panel in the incinerator room. Constant flow pumps (Model P-4000, E.I. DuPont de Nemours & Co., Inc., Wilmington, DE) were used to pull air through adsorption tubes (SKC Corp., Pittsburgh, PA) containing XAD-2®. Sampling durations were nominally 12 hours at a rate of about 240 mL/min. While two pumps were sampling, a second set of two pumps was being recharged. A background sample was taken at each location before incineration of waste was begun.

3.3.3 Monitoring

The officers of the M/T VULCANUS were responsible for taking and recording various data relating to incineration operations: temperatures, concentrations of O_2, CO_2, and CO in the stack gas; and waste feed rates. These data were accessible at any time, and the Chief Engineer made operating logs available on a daily basis, so that pertinent data could be recorded for reporting purposes.

4. TEST RESULTS

This chapter describes the results of sampling, monitoring, and chemical analysis activities that were performed onboard the M/T VULCANUS during this project. Many of the calculations are complex and/or lengthy; therefore, examples are provided in Appendix B, and the text is so noted.

4.1 DESCRIPTION OF THE WASTE

The waste characterization results given by Dr. Roger Henson, General Manager of CWM's facility at Emelle, AL, (personal communication with D. G. Ackerman on 21 July 1982) were as follows:

- Concentration of PCBs: 18.54 percent
- Concentration of Cl: 35.9 percent
- Heating value: 10,042 Btu/lb (5,562 cal/g)
- Specific gravity: less than 1.4

According to Dr. Henson, these were averages determined by analyses of shipments of waste to the facility at Emelle.

Each truckload of waste driven from Emelle, AL, to Chickasaw, AL, was accompanied by a manifest, which, among other data, showed the following: weight in pounds, volume in gallons, heat content in Btu/lb, percentages of PCBs and chlorine, date, load number, and driver's name. These data were entered into a form entitled "Oil Record Log" which was made available to the Chief Engineer and EPA. As each tank truck was loaded into the M/T VULCANUS, the cargo tank into which it was loaded was written in the "Oil Record Log". A total of 159 tank truck loads, including one load of diesel oil used to rinse the pumping system at the dock, was pumped into the M/T VULCANUS. Data from the "Oil Record Log" were used to characterize the waste (averages were weighted by the weight of each tank truck load) in each cargo tank and the entire cargo. Total weights and volumes were also computed. Results of this computation are given in Table 2.

TABLE 2. CALCULATED COMPOSITION OF THE CARGO

Tank No.	Weight lb	Spec. Grav. ml/g	Volume gal	Heat Content Btu/lb	PCB Content %	Cl Content %	Volume m^3	Weight mt
2P/S*	695,127	1.25	66,516	9,425	13.2	44.2	252	315
3P/S	552,380	1.16	57,209	9,997	19.5	39.6	216	251
4P/S	759,954	1.18	77,325	8,754	18.1	23.9	293	345
5P/S	639,340	1.26	61,024	10,104	25.3	40.8	231	290
1C	954,522	1.30	88,097	8,879	17.5	43.7	333	433
2C	1,375,230	1.10	150,571	10,867	19.6	26.2	570	624
3C	978,740	1.15	102,049	10,960	18.6	37.9	387	444
4C	966,680	1.20	113,680	8,634	19.9	33.7	430	438
5C	844,020	1.20	84,551	10,518	22.1	31.1	320	383
Total Cargo	7,765,993	1.16	801,022	9,858	19.3	34.8	3,032	3,523

*P = port, S = starboard, C = center

The weight of each tank truck load was measured and the volume calculated from the specific gravity. Weight is more accurate than volume, which varies with temperature. Individual volumes given in Table 2 differ slightly from corresponding values given in the Chief Engineer's voyage report (Appendix A). However, the Chief Engineer could measure only volume, and temperatures in the cargo tanks would be expected to be somewhat different from those in the tank trucks. The differences involved are small and do not change the ultimate destruction efficiencies. Analyses of samples of waste taken during the testing are described in Section 5.

4.2 WASTE FEED RATES

Feed rates for each test were calculated from the average feed rate and heat content of the entire cargo and individual heat contents measured on each sample of waste.* This calculation is illustrated in Appendix B.1. Table 3 presents the results.

TABLE 3. FEED RATES OF WASTE DURING THE TESTS

Test No.	Heat Content Btu/lb	Feed Rate mt/hr/incinerator
1	9,030	6.79
2	9,547	6.42
3	10,146	6.04
4	10,673	5.74
5	11,727	5.23
6	12,273	4.99
7	12,517	4.90
8	11,319	5.42
9	11,576	5.30
10	11,603	5.28

---

*Usually, feed rates are measured on a tank-by-tank basis, so that an individual feed rate can be measured for each test. However, during this project, motion of the ship made this method too inaccurate, and this alternative method for calculating feed rates for each test was employed.

4.3 VOLUMES OF STACK GAS SAMPLED

Table 4 presents various data relating to the combustion gas sampling effort.

TABLE 4. DATA FROM THE COMBUSTION GAS SAMPLING

Test No.	Date	Duration min	Volume Taken m^3[a]	Water Content % of Volume
1[b]	8-17-82	46	0.7092	3.0
2	8-18-82	26	0.3469	16.9
3[c]	8-19-82	120	2.0757	6.4
4[c]	8-19-82	120	1.9993	6.4
5[b]	8-20-82	120	1.9981	6.3
6	8-20-82	120	2.0669	6.6
7[c]	8-21-82	120	1.8906	7.3
8[c]	8-21-82	120	1.9527	11.3
9[c]	8-22-82	120	1.9382	9.0
10[b,c]	8-22-82	120	1.9076	8.4

[a] Dry cubic meters at 20°C and 1 atmosphere pressure. Sample calculation i Appendix B.2.

[b] Sampling train blanks were taken during these tests.

[c] Samples selected for analysis.

4.4 COMPOSITION OF THE COMBUSTION EFFLUENT

The Chief Engineer of the M/T VULCANUS was responsible for maintaining an operational log in the incineration room. In addition to other data, hourly readings from the combustion gas monitoring system were entered into this log which was available to the test crew. Average daily compositions of the combustion effluent were calculated from the operational log, waste feed rates, and composition of the waste (see Section 5.1 for results of analyses of the waste). Results of these calculations are given in Table 5. Of particular note is that combustion efficiencies averaged 99.99 percent. Example calculations are given, as indicated in footnotes to the table.

TABLE 5. CHARACTERIZATION OF THE COMBUSTION EFFLUENT[a]

Date	Test No.	O_2[b] %	CO_2[b] %	CO[b] ppm	HCl[c] %	H_2O[c] %	N_2[c] %	Excess Air[d]	Comb. Eff.[e]
8-17-82	1	9.2	10.1	16	3.2	7.4	71.8	79	99.98
8-18	2	9.9	9.4	9	2.9	8.4	71.6	90	99.99
8-19	3	9.9	9.4	8	2.6	7.2	72.8	90	99.99
8-19	4	9.9	9.4	8	2.4	8.2	72.4	90	99.99
8-20	5	10.7	8.7	8	1.9	7.5	73.3	105	99.99
8-20	6	10.7	8.7	8	1.7	7.6	73.6	105	99.99
8-21	7	10.2	8.9	8	1.5	8.5	73.1	96	99.99
8-21	8	10.2	8.9	8	1.8	9.4	72.5	96	99.99
8-22	9	10.2	9.0	8	2.0	8.1	73.3	96	99.99
8-22	10	10.2	9.0	8	1.9	8.3	73.0	96	99.99
8-23	--	9.7	9.5	7	f	f	f	87	99.99
8-24	--	10.4	8.8	8	f	f	f	99	99.99
8-25	--	10.1	9.1	7	f	f	f	94	99.99
8-26	--	10.6	8.6	7	f	f	f	103	99.99
8-27	--	10.2	9.0	6	f	f	f	96	99.99
8-28	--	10.1	9.3	6	f	f	f	94	99.99
8-29	--	10.1	9.3	6	f	f	f	94	99.99
Average	--	10.1	9.1	8	2.4	8.1	72.6	95	99.99

a. Compositions will generally not total to 100% because of uncertainties in the various measurements.
b. Averages of hourly readings for both incinerators.
c. Example calculation given in Appendix B.3.
d. Example calculation given in Appendix B.4.
e. Example calculation given in Appendix B.5.
f. Samples of waste were not taken, so that calculation of these quantities is not possible.

Table 6 presents calculated flow rates, wet and dry, of the combustion effluent. These values are used in the calculation of destruction efficiency.

TABLE 6. FLOW RATES OF COMBUSTION EFFLUENT[a]

Date	Test No.	Dry[b] m^3/hr	Wet[b] m^3/hr
8-17-82	1	57,847	62,449
8-18-82	2	62,524	68,268
8-19-82	3	64,288	69,300
8-19-82	4	65,207	71,002
8-20-82	5	67,499	72,948
8-20-82	6	69,484	75,223
8-21-82	7	64,679	70,715
8-21-82	8	61,806	68,214
8-22-82	9	65,984	71,774
8-22-82	10	64,669	70,484
Average		64,398	70,038

[a] Flow rate per incinerator.

[b] Volumes at 20°C and 1 atmosphere pressure. Sample calculation in Appendix B.3.

4.5 TEMPERATURES AND RESIDENCE TIMES

Readings of the wall thermocouples were recorded hourly. Averages (and standard deviations) of these temperatures were calculated on a daily basis and are presented in Table 7. The low range and standard deviations of these averages correlate well with the essentially constant combustion efficiencies and indicate a well controlled combustion process. Recalling that flame temperatures are 250 to 300°C higher than wall temperatures, the average flame temperature is estimated to have been 1550 to 1600°C (1303°C plus 250 or 300°C). An average residence time in the incinerators was calculated using the following relationship:

$$t = \frac{V}{\frac{CF}{3,600} \times \frac{T}{293}}$$

where V is the volume of an incinerator (133 m^3); CF is the flow rate of combustion effluent (average of 70,038 m^3/hr at 20°C and 1 atmosphere); 3,600 is the number of seconds in an hour; T is the flame temperature in degrees K; and 293 is the reference temperature (20°C or 293°K). Flame temperatures were calculated by adding the following to the wall temperature: 1) 273°C to convert from degrees Celsius to Kelvin and 2) 275°C, the average of how much hotter the flame temperature is than the wall temperature.

Using this relationship, the following pairs of residence time - flame temperature values were calculated:

Flame Temperature	Wall Temperature	Residence Time
1,648°K	1,100°C	1.5 seconds
1,748°K	1,200°C	1.4 seconds
1,848°K	1,300°C	1.3 seconds
1,948°K	1,400°C	1.2 seconds
2,048°K	1,500°C	1.1 seconds

An average residence time of 1.3 seconds was calculated from the equation and the average wall temperature of 1303°C.

TABLE 7. DAILY AVERAGE WALL TEMPERATURES

	Port Incinerator		Starboard Incinerator	
Date	$\bar{X}$, °C	s, °C	$\bar{X}$, °C	s, °C
8/17	1281	10	1290	17
8/18	1300	9	1313	12
8/19	1304	8	1302	8
8/20	1304	13	1311	9
8/21	1305	8	1311	14
8/22	1307	9	1312	8
8/23	1306	7	1309	16
8/24	1303	10	1303	11
8/25	1306	7	1306	9
8/26	1301	6	1306	10
8/27	1302	9	1304	10
8/28	1303	7	1301	14
8/29	1290	8	1300	8
Average of averages	1303			
Standard deviation	7			

*Averages of hourly readings of wall temperature. Flame temperatures are estimated to be approximately 250-300°C higher (2).

4.6 SAFETY AND PERSONNEL PROTECTION

Appendix B to permit HQ-81-002 (9) was a personnel protection plan which prescribed procedures for the ship's complement to follow in order to prevent contamination of the ship by the cargo and for monitoring, sampling, and analyzing samples in order to document adherence to the plan and levels of the cargo to which the complement may have been exposed. This plan was similar to the one used during the first PCB research burn (10,11) which was based on a plan developed by TRW Inc. for the Herbicide Orange disposal project (3).

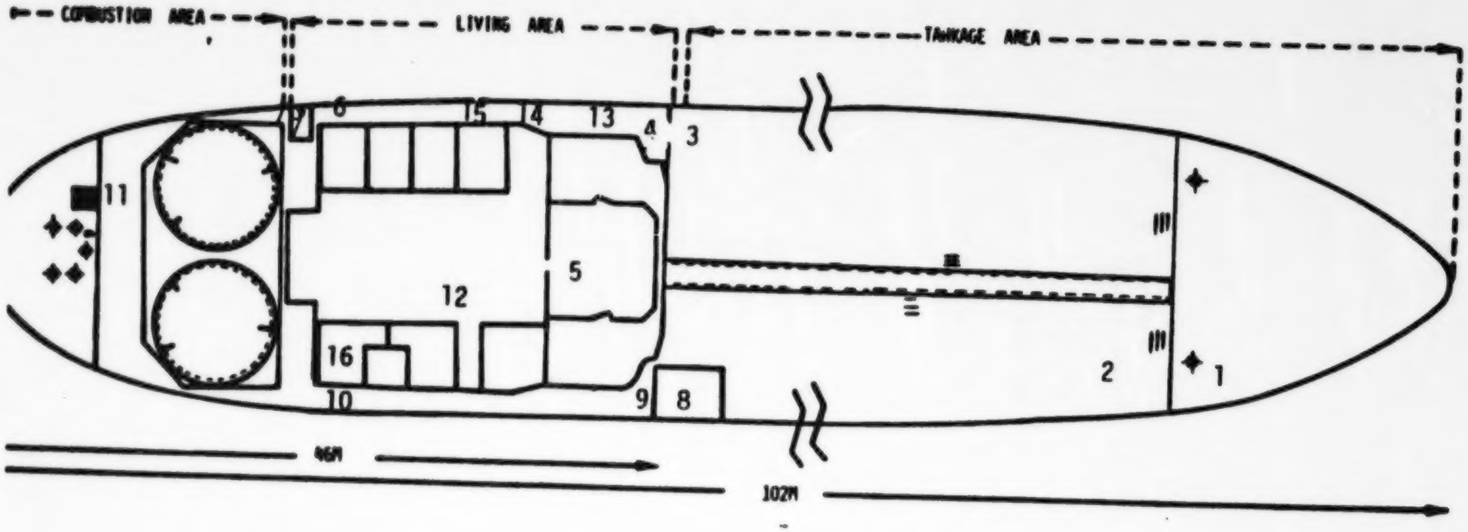
First, it is necessary to describe action-levels for PCBs that were employed during this test project. For wipe-samples, (Section 3.2) the detection of any amount of PCBs (detection limit was about 1 ng/wipe) in a living area was the action-level, and thorough cleaning and re-sampling was the response. The American Conference of Governmental Industrial Hygienists (ACGIH) had recommended Threshold Limit Values (TLVs) in air of 1 mg/m^3 for Aroclor 1248 and 0.5 mg/m^3 for Aroclor 1254 (20). A TLV is a time-weighted concentration for a substance in air that is considered safe for a worker exposed to it for 8 hours per day, 5 days per week, and 52 weeks per year. One method to convert TLVs to longer exposure periods is to decrease the TLV by a factor of 10 for each additional 8 hours of exposure. Thus, for 24-hour per day 7 days per week exposures on the M/T VULCANUS, the converted TLVs were:

- Aroclor 1248: 10 μg/m^3
- Aroclor 1254: 5 μg/m^3

Levels of PCBs in the work-space air were measured onboard the M/T VULCANUS during the first PCB research burn. The analyses showed no detectable amounts of PCBs, and detection limits were equivalent to the modified TLVs (10). Provision was not made for onboard analysis of samples of work space air taken during the second PCB research burn. Results of land-based analyses of these samples are given in Section 4.6.4.

4.6.1 Design of the Personnel Protection Plan

From an operational standpoint, the M/T VULCANUS, pictured in Figure 1 and shown schematically in Figure 12, consists of several functionally


COMBUSTION AREA
LIVING AREA
TANKAGE AREA
11
7
6
15
14
13
4
3
5
12
16
10
9
8
III
II
III
2
1
46M
102M

1. Foc'sle, top of stairs to main deck
2. Main deck, bottom of stairs to foc'sle
3. Main deck, entry to port passageway
4. Port passageway, just inside entry from main deck
5. Dining room floor
6. Port passageway, outside entry to incinerator room
7. Floorboards, inside entry to incinerator room
8. Main deck, entry to starboard passageway
9. Starboard passageway, entry to main deck
10. Starboard passageway, entry to incinerator room
11. Top of staircase from fantail
12. Bridge deck, landing in front of Second Off. head
13. Bridge wing, port side
14. Port passageway, entry to quarters
15. Middle port passageway
16. Floor, electrician's cabin

Figure 12. Schematic of M/T VULCANUS showing locations of wipe-samples.

discrete parts, each devoted to a specific operation such as waste storage, propulsion, combustion, and living quarters. The PCB-waste was handled in the storage and combustion areas. The living quarters, mess hall, galley, and recreation areas are located between the tankage area (forward) and the combustion room (aft). The location of the various functional portions of the ship are shown in Figure 12. The crew of 19 and the test and observation team of 4 were allowed to move freely about the ship in performing their duties and to return to the living area for meals, sleep, and recreation. This situation could have resulted in bringing toxic materials into the living quarters unless specific preventive procedures were established.

The personnel protection plan was designed to isolate the toxic material in the storage and combustion areas, protect personnel from possible contamination, and prevent the spread of the waste into other portions of the ship. Important considerations in the selection of this personnel protection plan were the:

- Confined nature of a shipboard operation
- Centralization of living quarters
- Percutaneous, ingestion, and inhalation paths of exposure

It was considered mandatory that working personnel be free of contamination before returning to eating and living facilities in order to avoid exposure of others not normally required to come in contact with the chemicals and to prevent additional exposure risk to themselves. A boundary-isolation method was selected as the most effective technique for excluding the wastes from those areas where personnel were concentrated. This concept appeared to have the greatest possibility of success with the least interference with working personnel. The objective was to isolate the PCBs within set boundaries, control access to those areas, and to eliminate carrying of the waste across the boundaries by onboard personnel. The ship was, therefore, divided into clean and contaminated areas with boundaries separating them.

- Three areas of the ship were considered to be probable sources of contamination:

  1) The main deck (forward) which covered the waste storage tanks through which protrude filling ports and access hatches (Butterworths) from the tanks

    2) The pump room, located below decks, aft of the waste storage area and below the living quarters

    3) The combustion room, which houses the lower portions of the two furnaces, the burners, and the incineration controls area

- One area was designated as free of contamination. This area contained:

    1) The bridge, with ship control and radio communication

    2) Living quarters for officers, crew, and test team

    3) The galley and combined mess hall/recreation room

In addition to defining the boundary-isolation method for controlling personnel movement, the personnel protection plan also defined criteria for interrupting the incineration to prevent exposure to the wastes. In brief, the personnel protection plan provided for interruption of incineration operations if:

- Conditions prevented keeping the plume off the ship
- Major spills occurred which could not readily be contained or cleaned
- Combustion efficiency fell below 99.9%

4.6.2 Implementation of the Personnel Protection Plan

The following goals were set for personnel protection onboard the M/T VULCANUS:

- Isolating the PCBs in working areas and excluding it from living areas by defining boundaries between dirty and clean areas
- Eliminating potential contamination carriers by providing for decontamination at these boundaries
- Locating and controlling contamination in a timely manner
- Controlling and monitoring incinerator operations to prevent workspace air concentrations of PCBs in excess of TLVs.

Concepts developed in the personnel protection plan were implemented by the test team and the ship's officers and crew. Implementation of the personnel protection procedures was effected by:

- A detailed briefing of ship and test personnel explaining the need for following the procedures by all personnel and the boundary-isolation concept

- Providing adequate and comfortable disposable protective clothing at the port exit from the combustion room

- Providing for an onboard analytical chemistry capability for detecting the spread of contamination past set boundaries

Briefing of the crew of the M/T VULCANUS was carried out at Chickasaw, AL. The briefing covered the toxic properties of the waste, the need for personal hygiene, and the effectiveness of safety procedures in preventing exposure. Test personnel were similarly briefed and were given pre- and post-program physical examinations.

Protective clothing consisted of cellulose fiber coveralls and plastic shoe covers. The coveralls were light, porous, comfortable, and inexpensive. They were discarded after each shift. Fresh coveralls were issued at the beginning of each shift. Shoe covers were available at the exits from the living quarters and at the port entrance to the combustion room. Disposal cans for used coveralls and shoe covers were provided just inside the port entry to the incinerator room. These cans were emptied daily and their contents burned in the incinerators.

There is a shower just off the port passageway outside the incinerator room (Figure 12). The shower was for use by personnel going off duty from the combustion room or from other contamination sources, such as the pump room or storage area were required to use this shower.

An onboard analytical chemistry capability was discussed in Section 3.2. An extensive sampling and monitoring program was followed to detect any possible spread of contamination or excessive workspace air levels of waste:

- Areas critical with respect to the spread of contamination or likely to be sources of contamination were wiped with filter discs and then analyzed.

- Workspace air samples were taken by personnel monitor pumps and adsorption tubes for land-based analysis.

4.6.3 Results of Analyses of Wipe-Samples

Figure 12 shows locations at which wipe-samples were taken. Results of analyses of these samples are given in Table 8 and show that good segregation of the waste was achieved and that the living quarters area was kept free of the waste.

TABLE 8. RESULTS OF ANALYSES OF WIPE-SAMPLES

Location	8-17	8-18	8-19	8-20	8-21	8-22	8-23	8-24	8-25	8-26	8-27	8-28	8-29	8-30
1	Neg[a]	---[b]	Neg	---	Neg	Neg	---	Neg	---	Neg	Neg	Neg	---	---
2	Neg	---	---	---	---	---	---	---	---	---	---	---	---	---
3	Neg	---	Neg	---	Neg	Neg	---	Neg	---	Neg	Neg	Neg	---	---
4	Neg	---	Neg	---	Neg	Neg	---	---	---	---	---	---	---	---
5	Neg	---	Neg	---	Neg	Neg	---	Neg	---	Neg	Neg	Neg	---	---
6	Neg	---	Neg	---	---	Neg	---	Neg	---	Neg	---	---	---	---
7	Neg	---	Neg	---	---	Neg	---	Neg	---	---	Neg	Neg	---	---
8	Neg	---	---	---	---	---	---	---	---	---	---	---	---	---
9	---	---	Neg	---	---	---	---	---	---	---	---	---	---	---
10	---	---	Neg	---	---	---	---	Neg	---	---	---	---	---	---
11	---	---	---	---	Neg	---	---	---	---	---	---	---	---	---
12	---	---	---	---	---	---	---	---	---	---	---	---	---	---
13	---	---	---	---	Neg	---	---	---	---	---	---	---	---	---
14	---	---	---	---	---	---	---	---	---	---	---	---	---	---
15	---	---	---	---	---	---	---	---	---	---	---	---	---	---
16	---	---	---	---	---	Neg	---	Neg	---	Neg	---	---	---	---
17	---	---	---	---	---	Neg	---	Neg	---	---	---	Neg	---	---
18	---	---	---	---	---	Neg	---	---	---	Neg	---	---	---	---

a. "Neg" means that patterns of GC peaks corresponding to Aroclors 1254 and 1260 were not found.
b. "---" means a sample was not taken at the location and date indicated.

4.6.4 Results of Analyses of Work-Space Air Samples

Each of the adsorption tubes selected for analysis was extracted with hexane for 45 minutes, and the extract was analyzed by GC/ECD for PCBs (Aroclor® 1254 and 1260). No PCBs were detected. Maximum possible concentrations of individual PCB compounds ranged from <0.2 µg/m^3 to <0.4 µg/m^3. These values were calculated from the detection limit (50 pg/µL), the volume of extract (1 mL), and the volumes of work space air sampled (140 to 230 liters at 20°C and 1 atmosphere).

5. ANALYTICAL RESULTS

5.1 INTRODUCTION

All samples collected onboard the M/T VULCANUS were delivered to TRW's laboratory in Research Triangle Park, NC by the TRW personnel responsible for the sampling. Samples were immediately inspected, checked against the accompanying sample manifest, and given a laboratory control number.

A total of ten tests was performed during the project, six of which were selected for analysis. The six tests were selected so as to best represent the waste contained in the various cargo tanks of the ship. Two "blank" trains were also included for analysis. The test numbers and corresponding tank numbers are given below:

Test No.	Tank No.
3	1C and 5C
4	5C
5-blank	—
7	2C
8	2C and 4C
9	3C
10	3C
10-blank	—

Each sampling train contained 6 individual components that were recovered as samples for subsequent analysis. The individual samples were as follows: the probe rinse (also including the rinses of the first three impingers and the Teflon® heat-traced line); the contents of the first three impingers; the Florisil® trap; the XAD-2® trap; the contents of the 4th and 5th impingers; and the silica gel. The silica gel associated with all tests were weighed and the data recorded for determination of moisture in the gas samples. The pH of the 4th and 5th impinger solutions of the selected tests was determined and considered only as a general, qualitative observation. These two impingers were for the protection of the pump and metering system. Four of the 6 individual components associated with each test (the probe rinse, the contents of the first three impingers, and the Florisil® and XAD-2® sorbents) were analyzed for PCBs, CBs, TCDFs, and TCDDs.

Upon completion of the sample "log-in" effort and before any sample preparation steps, probe rinses, contents of the first three impingers and the Florisil® and XAD-2® sorbents of each sample train were fortified with the labeled ^{13}C - 2,3,7,8-TCDD internal standard by a member of the EPA's Advanced Analysis Techniques Branch, EMSL/RTP in the presence of the EPA project officer. The labeled internal standard was incorporated to determine and validate the analytical methodology and efficiency for the determination of TCDFs and TCDDs in each sample.

Quality Assurance (QA) samples (hexane/acetone, water, Florisil®, and XAD-2®) were fortified with the labeled internal standard and with 0, 1, 2, or 4 ng of 2,3,7,8-TCDF and 2,3,7,8-TCDD. One raw waste sample was used for preparation of four QA samples, i.e., two of the QA samples were not fortified and were used as blanks, and two of the QA samples were fortified with 50 ng of 2,3,7,8-TCDF and 30 and 40 ng 2,3,7,8-TCDD, respectively. Raw waste samples, including the four QA samples, were fortified with the labeled internal standard by UNL personnel at Lincoln, NE. All QA samples were assigned TRW identification numbers and interspersed among the actual test samples in a "blind" fashion, i.e., there was no way for personnel at UNL or EPA/EMSL/RTP to distinguish QA sample from actual test sample.

All test samples and QA samples, except the raw waste samples, were subjected to specific extraction procedures by TRW/RTP. Each sample extract was split, and one-half was retained by TRW for analysis of PCBs and CBs. The other half of each sample extract and samples of raw waste were flown directly to Lincoln, Nebraska in a private aircraft and transferred to an authorized representative of the Chemistry Department of UNL utilizing chain of custody procedures. Raw waste samples were then fortified with ^{13}C - 2,3,7,8-TCDD and subjected to specific extraction procedures by UNL (see Appendix H). Extracts derived from the UNL and TRW extraction procedures were then subjected to specific UNL clean-up procedures for isolation of TCDFs and TCDDs. The extracts were then "split" and subjected to low and high resolution gas chromatography - high resolution mass spectrometric methods of analysis for determination of TCDFs and TCDDs by UNL and EPA/EMSL/RTP.

As described in Section 5.5, a QA-contractor to EPA prepared a set of QA samples and submitted them to TRW for analysis of PCBs.

5.2 REAGENTS AND CHEMICALS

5.2.1 Solvents

All solvents (hexane, acetone, methanol, and water) used in this study were pesticide quality, Burdick and Jackson "Distilled-in-Glass"® grade. The solvents used during the sampling effort were from the same lots as the solvents used in the laboratory analyses. Each solvent was screened by gas chromatography/electron capture detection (GC/ECD) before use.

5.2.2 Chemicals

Sodium sulfate, used for removing water from organic solvents before concentration, was prepared by thoroughly rinsing with hexane and drying at 110°C overnight. It was screened for interfering impurities by being incorporated into the solvent/glassware "blanking" scheme.

Alumina, which was used in sample cleanup, was activated by adding 3% moisture, by weight, and allowing to stand for 1.5 hours before use. Appropriate blanks were made by flushing a column of alumina with the eluting solvent (hexane), concentrating, and analyzing in the same manner utilized for a sample.

5.3 SAMPLE PREPARATION

As noted in Section 5.1, all stack gas samples were fortified by personnel from EPA with internal standards. Personnel from TRW also fortified each sample with 2,3,6-tribromobiphenyl (TBB) to a level of 180 ng or 720 ng per sample. The internal standards were added to permit the analysts to measure efficiencies of recovery of sought for compounds through the analytical scheme and to validate the overall methodology. ^{13}C-labeled-2,3,7,8-TCDD was selected because it would behave during the chemical analysis exactly like 2,3,7,8-TCDD but would be distinguishable from it by the mass spectrometer. Similarly, it was expected to behave very much like 2,3,7,8-TCDF. TBB was selected because its chemistry is similar to that of a PCB, it responds instrumentally much like a PCB, it was not expected to be present in the samples, and its molecular weight is great enough that interferences with its ions are rarely encountered (21). Table 9 gives the concentration to which each sample was spiked and other sample workup parameters.

5.3.1 Impinger Contents (Container No. 1)

The physical properties (color, consistency, presence of solids) were noted and then each sample was fortified. The initial volumes (Table 9) and pH (Table 10) were measured, and they were brought to known volume with deionized, organic-free water. A 10-mL aliquot was removed for determination of chloride by ion chromatography, as discussed in Section 5.4.3. Without adjusting the pH, each sample was transferred to a 1000 mL separatory funnel and extracted with three separate 100 mL aliquots of hexane, the first of which also contained acetone and hexane rinses of the sample container. The resulting hexane extracts were combined, brought to 500 mL, and split into halves. One half of each sample was transferred to an amber jar with a Teflon®-lined lid for shipment to the University of Nebraska. The second half was transferred to a Kuderna-Danish (K-D) evaporator after filtering through sodium sulfate to remove any residual water. The extracts were reduced in volume to approximately 10 mL in the K-D and further reduced in volume to 4 mL in a graduated 15 mL conical screw cap centrifuge tube by evaporating with a gentle stream of pure nitrogen. These extracts were analyzed by the procedures discussed in Section 5.4.

5.3.2 Hexane and Acetone Rinses of Probe, Teflon® Line, and Impingers (Container No. 2)

The physical properties were noted, and each sample was fortified. Initial volumes were measured, and they were brought to known volume (either 2000 mL or 2500 mL) with hexane. Each sample was then split into two equal portions, one-half being shipped to Nebraska. After a 10-mL aliquot had been removed, the second half of each sample was transferred to a K-D evaporator as described in Section 5.3.1. The 10 mL aliquots that were removed were

TABLE 9. SAMPLE WORK-UP PARAMETERS

Run # - Sample ID[1]	Volume as Received (mL)	Final Volume After Dilution (mL)	Volume Retained by TRW (mL)	Concentration Volume (mL)	TBB Level[2] Expected in TRW Portion (ng)	Comments
Run 3						
PR	2280	2500	1250	15	360	Light Green & Clear
IE	457	500	250	3	360	Light Green & Clear
XE	---	500	250	4	90	
FE	---	500	250	4	90	
Run 4						
PR	2240	2500	1250	15	360	Light Green & Clear
IE	415	500	250	4	360	Light Green & Clear
XE	---	800	400	4	360	
FE	---	500	250	4	360	
Run 5[3]						
PR	1780	2000	1000	15	360	
IE	383	500	250	4	360	
XE	---	1000	500	4	360	
FE	---	500	250	4	360	
Run 7						
PR	2290	2500	1250	15	360	Light Green & Clear
IE	437	500	250	4	360	Light Green & Clear
XE	---	800	400	4	360	
FE	---	500	250	4	360	
Run 8						
PR	2210	2500	1250	15	360	Light Green & Clear
IE	500	500	250	4	360	Light Green & Clear
XE	---	700	350	4	360	
FE	---	500	250	4	360	
Run 9						
PR	1850	2000	1000	15	360	Light Green & Clear
IE	447	500	250	4	360	Light Green & Clear
XE	---	1000	500	4	360	
FE	---	500	250	4	360	
Run 10						
PR	1930	2000	1000	15	360	Light Green & Clear
IE	443	500	250	4	360	Light Green & Clear
XE	---	800	400	4	360	
FE	---	500	250	4	360	
Run 11[3]						
PR	1690	2000	1000	15	360	
IE	395	500	250	4	360	
XE	---	500	250	4	180	
FE	---	500	250	4	90	

[1] PR = Probe Rinse, also includes Line Rinse & Impinger Rinse;
ment of two of th IE = Impinger Extract;
XE = XAD-2 Extract;
FE = Florisil Extract.

[2] These values represent one-half the total, original spike, as each sample was split in half.

[3] Blank Runs.

TABLE 10. pH OF IMPINGER SOLUTIONS

Test No.	1st, 2nd, 3rd Combined	4th & 5th Combined
3	0.1	1.2
4	0.1	1.35
5-blank	6.2	9.0
7	0.1	1.25
8	0.1	1.25
9	0.1	1.2
10	0.1	1.15
10-blank	5.2	7.1

extracted with 10 mL of water which was analyzed for chloride ion as discussed in Section 5.4.3. The remaining sample was concentrated to approximately 10 mL in the K-D evaporator. At this point the samples had become black, opaque, and visible solid material was clinging to the glass walls of the K-D evaporator. A method was developed to recover the sought-for species from these samples. It is described in subsequent paragraphs.

The liquid portions of these samples were then transferred to centrifuge tubes. A 1-mL aliquot of methanol was added to rinse to the first K-D. The black, solid material immediately dissolved, indicating that a great majority of the sample was quite polar in nature. Each K-D evaporator was then rinsed several times with methanol, and the rinses were added to the corresponding centrifuge tube until the total volumes were 15 mL. Thus, any PCBs and CBs present were contained in a mixture of hexane and methanol.

Because it was desirable to have PCBs and CBs in hexane only, the following experiments were performed to accomplish this transfer. First, an aliquot of hexane (2.5 mL) and methanol (5 mL) were mixed into a single phase for a total volume of 7.5 mL. Second, a 5-mL aliquot of water was added and the mixture vigorously shaken. Two phases resulted, and the top layer was the 2.5 mL portion of hexane.

This experiment was then performed on a larger scale in a 125 mL separatory funnel using the probe rinse sample from Test 1. (Test 1 was valid but was terminated prematurely because of difficulties associated with the formation of sodium carbonate in the 4th and 5th impingers. Because the volume of gas sampled was small, this test was not a primary choice for analysis and was, therefore, used for these preliminary experiments.) Part of the sample was subjected to this procedure with a spike added that contained ten individual PCBs (A mixture containing one each of the mono-through the decachloro-biphenyls, Supelco, Inc., Bellefonte, PA), and part of the sample was subjected to this procedure with no added spike. The procedure required the transfer of 15 mL sample from the centrifuge tube to the separatory funnel, followed with 30 mL of methanol rinse and 25 mL of hexane rinse. A 45 mL aliquot of water was then added and the contents vigorously shaken for 5 minutes. The hexane layer (25 mL) was drawn off. This extraction was repeated two additional times with 25 mL aliquots of hexane, and each extract was filtered through anhydrous sodium sulfate into a K-D evaporator. The contents were reduced in volume to 4 mL and analyzed by gas chromatography with electron capture detection (GC/ECD). The results indicated that 98% of the added PCBs had been transferred from the methanol-water phase into the hexane. The six probe rinse samples and two blanks were then subjected to the procedure described above.

Each probe rinse sample was then analyzed by GC/ECD, and it was found that the samples contained numbers of components that could possibly cause interference during gas chromatography with high resolution mass spectrometric (GC/HRMS) detection. Therefore, the samples were subjected to a second cleanup step utilizing activated alumina. The probe rinse from Test 1 was again used for a preliminary experiment. The 4 mL concentrated sample, described above, was added to the top of an 18 cm long x 2.5 cm column (covered with about 2 cm of sodium sulfate) after it had been washed with two 50-mL aliquots of hexane. The sample was eluted with three 50-mL aliquots of hexane and collected directly into a K-D evaporator. The contents were concentrated to 4 mL and analyzed.

The recovery of the added PCBs was 89%. The six probe rinse samples and two blanks were subjected to this cleanup/concentration step and then analyzed by the procedures described in Section 5.4. The six probe rinse samples each had a distinctive pale green color which remained on the column but which had separated into at least three separate bands. The hexane fraction containing the PCBs was clear and colorless.

5.3.3 Contents of 4th and 5th Impingers (Container No. 3)

The contents of the 4th and 5th impingers were of secondary importance, and consquently very little analytical work was performed. The volume of each sample was estimated to be approximately 900 mL, and no particulate matter was apparent. The pH of each sample was determined, and the values are given in Table 10. The samples were stored in their original containers.

5.3.4 Florisil® and XAD-2® Adsorbents

The Florisil® sorbent was distinctively pale green in color, and both the Florisil® and XAD-2® were obviously wet from entrained moisture during sampling. The sorbents were spiked directly with ^{13}C-2,3,7,8-TCDD and TBB before removal from the traps. Each sorbent material was then transferred to an all-glass Soxhlet extractor, which was charged with approximately 300 mL of hexane, and extracted for 20 hours at a cycle rate of 10-14 exchanges per hour. Because of the criticality of this step, the extractions were physically monitored continuously. Upon completion of the extraction, the samples were brought to a known volume and split as described in previous sections.

Because of the "wet" condition of the sorbents, they were packed loosely in the thimbles in an effort to facilitate contact with the hexane. However, the action of the Soxhlets gave the appearance of poor solvent-sorbent contact which could cause potentially poor extraction efficiencies. In order to determine if this was the case, the Florisil® from Test 3 was re-extracted with hexane for an additional 20 hours. A screen by GC/ECD of the first extract showed an excellent recovery of TBB. The analysis of the second extract showed no peaks. It was concluded that these extractions were quantitative.

The portion of each sample retained by TRW was concentrated to 4 mL in a K-D evaporator and analyzed as discussed in Section 5.4.

5.3.5 Silica Gel

The silica gel samples from all ten tests were weighed to determine the moisture content to be used for sample volume corrections. The results are given in Table 11.

TABLE 11. GAIN OF WATER BY SILICA GEL SAMPLES

Test No.	Gain, g	Test No.	Gain, g
1	6.5	6	30.4
1-blank	0.7	7*	31.9
2	7.8	8*	24.0
3*	41.5	9*	33.7
4*	22.9	10*	30.4
5	26.0	10-blank*	-0.6
5-blank	0.8	10-blank-D+	0.5

*Samples from these tests were selected for analysis.

+This was a duplicate of samples from test 10-blank.

5.3.6 Raw Waste

Approximately 500 mL of raw waste corresponding to each test was received for analysis. Each bottle was agitated to effect homogeneity before removing an aliquot. Three separate sets of aliquots of raw waste were prepared and distributed for analysis. The first set, consisting of approximately 50 mL of each of the ten individual waste samples, a composite of all ten wastes collected, and a composite of 6 wastes (sampled during the 6 tests selected for analysis) was shipped to an independent testing laboratory for proximate/ultimate analyses (carbon, hydrogen, nitrogen, chlorine, sulfur, and oxygen), ash, specific gravity, and BTU/lb. These results are given in Table 12.

TABLE 12. RESULTS OF PROXIMATE/ULTIMATE ANALYSES OF SAMPLES OF WASTE

Test Number	%C	%H	%Cl	%N	%S	%O	% Ash	Specific Gravity, 71°F	Heat Content Btu/lb
1	44.89	4.35	43.63	0.08	0.04	6.93	0.08	1.30	9,030
2	44.37	4.87	45.02	0.06	0.04	5.38	0.26	1.22	9,547
3	47.32	5.03	43.51	0.06	0.04	3.81	0.23	1.23	10,146
4	48.71	5.21	43.12	0.06	0.04	2.71	0.15	1.20	10,673
5	53.71	5.25	39.62	0.03	0.06	1.33	0.00	1.19	11,727
6	55.39	5.67	38.10	0.06	0.12	0.63	0.03	1.17	12,273
7	57.27	6.58	32.87	0.03	0.11	3.18	0.07	1.11	12,517
8	49.55	6.80	32.87	0.03	0.02	10.51	0.22	1.13	11,319
9	51.08	6.06	40.95	0.03	0.10	1.63	0.15	1.16	11,576
10	49.45	6.13	37.75	0.03	0.04	6.36	0.24	1.14	11,603
C-6[a]	51.70	5.87	37.85	0.08	0.03	4.35	0.12	1.17	11,050
C-10[b]	50.22	5.51	38.57	0.06	0.02	5.52	0.10	1.19	10,892

[a] Composite of samples from Tests 3, 4, 7, 8, 9, and 10.

[b] Composite of samples from all ten tests.

A second set of aliquots (10 mL) of each of the 6 waste samples (sampled during the 6 tests selected for analysis) was bottled and shipped to the University of Nebraska for analysis.

A third set of aliquots was prepared for GC/ECD and GC/HRMS analysis by serially diluting a 1 mL portion of each of the six raw waste samples with hexane (by a factor of 25,000 for GC/ECD and 10,000 for GC/HRMS). The final dilution was analyzed without any cleanup. The analytical procedures and results are given in Section 5.4.

5.4 ANALYTICAL PROCEDURES AND RESULTS

All samples were first screened by GC/ECD to determine relative amounts of compounds before performing more detailed analyses by GC/HRMS and GC/ECD. GC/HRMS was the primary choice for qualitative and quantitative determinations in this work, and values for destruction efficiency presented in Chapter 6 are based on those results. All samples (including QA samples) were also analyzed by GC/ECD using the same standards as used during the analyses by GC/HRMS. The results of both methods are presented below.

5.4.1 GC/HRMS

Analyses by GC/HRMS were performed under subcontract to Harvey Laboratories, Inc., of Charlottesville, Virginia. Upon completion of sample preparation steps, all samples were hand delivered. Preliminary information obtained through screening by GC/ECD accompanied the samples.

The analysis protocol called for the GC/MS analysis to be performed in either the selected ion monitoring mode or the total scan mode. The latter was selected for this work because this approach allows the analyst to obtain a reconstructed ion chromatogram for additional interpretation in the event that interfering species were present, or that supplemental data are required. Detection limits of the GC/HRMS in the total scan mode were adequate to achieve the desired destruction efficiencies.

A description of the instrumentation and conditions is given below:

Mass Spectrometer

- VG (VG Analytical Ltd., Cheshire, England) Micro Mass Model 70/70 H, (high sensitivity model)
- VG 2035 data system
- Scan range/rate - 600-60 AMU at 500 m-sec/decade

Gas Chromatograph

- Varian (Varian Associates, Inc., Palo Alto, CA) Model 3700, 30-m, SE-54 coated on fused silica capillary; on-column injection, typically 1-2 μL
- Temperature program - 100° to 270°C @ 5°/min
- Carrier - helium, 0.85 cc/min

5.4.1.1 Analyses of Standards. PCB standards were purchased from Ultra Scientific, Inc., Cambridge, MA. A total of 28 isomers was selected which included three each of the monochloro- through the nonachloro- and the single decachlorobiphenyl. Names of these PCBs are given in Table 13. Three

TABLE 13. PCB ISOMERS USED TO DETERMINE RESPONSE FACTORS

	PCB Stock Solution		
	1	2	3
Monochloro	2	3	4
Dichloro	2,2'	2,4	2,6
Trichloro	2',3,4	2,4,6	2,4,4'
Tetrachloro	2,2',6,6'	3,3',4,4'	2,2',4,4'
Pentachloro	2,2',4,6,6'	2,3,4,4',6	2,3,3',5,6
Hexachloro	2,2',3,3',6,6'	2,2',4,4',6,6'	2,2',3,5,5',6
Heptachloro	2,2',3,4,5,5',6	2,2',3,4,4',5,6	2,2',3,3',4,4',6
Octachloro	2,2',3,3',4,5,6,6'	2,2',3,3',4,4',5,5'	2,2',3,3',5,5',6,6'
Nonochloro	2,2',3,3',4,5,5',6,6'	2,2',3,3',4,4',5,5',6	2,2',3,3',4,4',5,6,6'
Decachloro	2,2',3,3',4,4',5,5',6,6'	--------------------	--------------------

stock solutions were prepared in which each solution contained only one isomer of a given chlorine number group (i.e., Solution No. 1 contained only one monochloro-, dichloro- ....biphenyl isomer). The first solution contained ten isomers, while the other two contained only nine each (there is only one possible decachlorobiphenyl compound). These solutions were prepared at a concentration of 5 mg/100 mL in hexane and diluted as necessary.

Each solution was analyzed a total of three times at two different concentrations, and the average response factor for each isomer was calculated. Therefore, the analysis of each of the three standard solutions resulted in 9 or 10 separate response factors, depending on the standard solution. These response factors from each of the three standard solutions were then averaged, resulting in a single average molar response factor for the monochloro-, the dichloro-, ...biphenyls.

The measurement of individual peak areas for calculating molar response factors was approached in three ways: the most intense ion area, total ion area, and the low mass area. All three approaches were tried on one standard, and the results were within ±10% for any chlorine number group. No major advantage was gained from using one method over another. However, the lowest mass (first ion in a cluster) was generally the easiest to determine, and this was the method chosen.

Relative Molar Response Factors (RMRF) were then determined for each chlorine number group by relating the average response factors to that of TBB which was co-injected with each standard PCB solution. These RMRFs for each chlorine number group were then used to quantitate the PCBs based on the levels of TBB known to have been spiked into each sample.

TBB levels in each sample were determined by co-injection of a known amount of d_{12}-chrysene (perdeuterated) with each sample and comparing that response with that of d_{12}-chrysene co-injected with a known level of TBB.

Based on the qualitative identification of each peak in a sample (identity as a mono-, di-, tri-, ...chlorobiphenyl isomer), the areas under each monochloro-, dichloro-, ...biphenyl peak were summed. This approach to the quantitation of the PCBs resulted in up to 10 separate values (and a total) for any one sample.

In addition to PCBs, chlorobenzenes were identified and quantitated in the raw waste and corresponding stack gas samples. Relative Molar Response Factors were determined for all chlorobenzene compounds (all compounds was purchased from Ultra-Scientific, Inc.), and average values were calculated for each chlorine number group. Results of the analyses of the raw waste samples for PCBs and chlorobenzenes are given in Tables 14 and 15, respectively.

TABLE 14. CONCENTRATION OF PCBs IN THE RAW WASTE BY GC/HRMS
(by Chlorine Isomer Group, mg/mL)

Test #	Cl_1	Cl_2	Cl_3	Cl_4	Cl_5	Cl_6	Cl_7	Cl_8	Cl_9	Cl_{10}	Total
3	0.16	4.94	20.0	29.7	41.7	103	69.5	14.0	0	0	283
4	0.19	5.27	20.5	30.4	53.5	113	108	21.5	0	0	352
7	0	5.69	27.5	36.2	49.5	105	98.8	22.3	0	0	345
8	0	5.21	21.6	24.2	38.6	87.2	79.0	10.7	0	0	267
9	0.28	3.28	19.3	31.2	53.7	114	109	21.7	0	0	352
10	0	4.58	16.0	28.5	49.7	101	92.0	22.0	0	0	314

TABLE 15. CONCENTRATION OF CHLOROBENZENES IN THE RAW WASTE BY GC/HRMS
(by Chlorine Isomer Group, mg/mL)

Test #	Cl_1	Cl_2	Cl_3	Cl_4	Cl_5	Cl_6	Total
3	2.17	1.16	37.11	26.29	6.34	10.91	83.98
4	1.04	1.2	38.98	24.9	7.85	13.2	87.17
7	0.21	2.47	32.39	29.27	6.83	6.38	77.55
8	3.06	1.05	36.11	19.6	4.46	5.53	69.81
9	1.15	1.0	36.3	25.3	8.4	11.5	83.65
10	0	1.44	22.58	31.08	10.58	11.05	76.73

5.4.1.2 Analyses of Samples. The four stack gas samples associated with each of the 6 tests were analyzed for PCBs and chlorobenzenes. No compound of interest was detected in any sample at the minimum detectable limit (MDL). Because of the overall higher level of interferences in the probe rinse samples, the instrumental MDL was established at 100 picograms (pg, 10^{-12}g) of compounds per μl injected. Because the extracts of the impingers, Florisil®, and XAD-2® had lower levels of interferences, the instrumental MDL was 25 pg per μL injected.

In an effort further to reduce the MDL of the method, 100 μL of the impinger extract of each test was combined with 100 μL each of the Florisil® and XAD-2® extracts of the same test. This 300 μL "combination" sample was reduced in volume to 100 μL. The "combination" samples were re-analyzed. Again, no PCB or CB was detected. This procedure of combining the three extracts (of impingers, XAD-2®, and Florisil®) reduced the MDL of the method from 75 pg/μl to 25 pg/μl injected per compound. The MDL of the overall method (analysis of probe rinse and "combination" sample) was 125 pg/μl (100 pg/μl plus 25 pg/μl) for any PCB or CB compound. These MDL values are shown in Tables 16 and 17.

Table 16 also presents recoveries of TBB spiked into the original samples, quantitated by both GC/MS and GC/ECD. The recoveries are generally high and reproducible. Because of the similar chemical behavior of TBB and PCBs, these recoveries are indicative of the overall effectiveness of the sample extractions and validity of the methodology. If any PCBs had been present in the original samples, they would have been detected if present at levels at or above the MDL. The agreement between the GC/HRMS and GC/ECD results is generally good. In some instances, the GC/ECD results are higher, and is probably from occluded peaks.

Table 16. MINIMUM DETECTION LIMITS OF THE METHOD FOR PCBs BY GC/HRMS (pg/µl) AND TBB RECOVERIES

Run # 1 Sample ID	Cl_1	Cl_2	Cl_3	Cl_4	Cl_5	Cl_6	Cl_7	Cl_8	Cl_9	Cl_{10}	TBB Recovery, % GC/MS	TBB Recovery, % GC/ECD
Run 3												
P.R.	100	100	100	100	100	100	100	100	100	100	---[5]	24[3]
I.E.	25	25	25	25	25	25	25	25	25	25	82	---[5]
X.E.											91	95
F.E.											99	130
Run 4												
P.R.	100	100	100	100	100	100	100	100	100	100	111	129
I.E.	25	25	25	25	25	25	25	25	25	25	90	---[5]
X.E.											87	---[5]
F.E.											90(87[4])	---[5]
Run 5[2]												
P.R.	100	100	100	100	100	100	100	100	100	100	112	113
I.E.	25	25	25	25	25	25	25	25	25	25	89	87
X.E.											98	70
F.E.											92	87
Run 7												
P.R.	100	100	100	100	100	100	100	100	100	100	89	69
I.E.	25	25	25	25	25	25	25	25	25	25	83	87
X.E.											97	87
F.E.											83	88
Run 8												
P.R.	100	100	100	100	100	100	100	100	100	100	109	89
I.E.	25	25	25	25	25	25	25	25	25	25	102	83
X.E.											89	118
F.E.											79	116
Run 9												
P.R.	100	100	100	100	100	100	100	100	100	100	---[5]	86
I.E.	25	25	25	25	25	25	25	25	25	25	91	70
X.E.											96	87
F.E.											91	90
Run 10												
P.R.	100	100	100	100	100	100	100	100	100	100	98	90(100[4])
I.E.	25	25	25	25	25	25	25	25	25	25	90	98
X.E.											73	103
F.E.											97	108
Run 11[2]												
P.R.	100	100	100	100	100	100	100	100	100	100	97	88
I.E.	25	25	25	25	25	25	25	25	25	25	83	80
X.E.											62[6]	87
F.E.											71[6]	87

[1] P.R. = Probe Rinse (also includes Transfer Line Rinse and Impinger Rinses);
I.E. = Impinger Extract;
X.E. = XAD-2 Extract;
F.E. = Florisil Extract.

[2] Blank Run

[3] Sample Losses

[4] Duplicate Analysis

[5] Interferences Prevented Quantitation

[6] Spiking Level Too Low To Accurately Quantify

Table 17. MINIMUM DETECTION LIMITS OF THE METHOD FOR CHLOROBENZENES BY GC/HRMS (pg/μl)

Run # - Sample ID	Cl_1	Cl_2	Cl_3	Cl_4	Cl_5	Cl_6
Run 3						
P.R.	100	100	100	100	100	100
I.E.	25	25	25	25	25	25
X.E.						
F.E.						
Run 4						
P.R.	100	100	100	100	100	100
I.E.	25	25	25	25	25	25
X.E.						
F.E.						
Run 5[2]						
P.R.	100	100	100	100	100	100
I.E.	25	25	25	25	25	25
X.E.						
F.E.						
Run 7						
P.R.	100	100	100	100	100	100
I.E.	25	25	25	25	25	25
X.E.						
F.E.						
Run 8						
P.R.	100	100	100	100	100	100
I.E.	25	25	25	25	25	25
X.E.						
F.E.						
Run 9						
P.R.	100	100	100	100	100	100
I.E.	25	25	25	25	25	25
X.E.						
F.E.						
Run 10						
P.R.	100	100	100	100	100	100
I.E.	25	25	25	25	25	25
X.E.						
F.E.						
Run 11[2]						
P.R.	100	100	100	100	100	100
I.E.	25	25	25	25	25	25
X.E.						
F.E.						

[1] P.R. = Probe Rinse (also includes Transfer Line Rinse and Impinger Rinses);
I.E. = Impinger Extract;
X.E. = XAD-2 Extract;
F.E. = Florisil Extract.

[2] Blank Run

The m/z for the PCBs of interest and for TBB which were used for quantitation are given below:

Chlorine Number Group	m/z
Cl_1	188
Cl_2	222
Cl_3	256
Cl_4	290
Cl_5	324
Cl_6	358
Cl_7	392
Cl_8	426
Cl_9	460
Cl_{10}	494
TBB	388

5.4.2 GC/ECD

Analysis by GC/ECD was used first as a screening technique to gain preliminary information about the samples, and then as a secondary quantitative technique. A description of the instrumentation and conditions is given below:

- Varian Model 6000 GC, ^{63}Ni-ECD
- Varian Vista 401 Data Station
- Column, SE-54 coated on a 30-m fused silica capillary, nitrogen carrier gas, hot needle injection, typically 1-2 μL, split ratio 1:10
- Temperature program - 100° to 270°C at 3°C/min, held at 270°C until all peaks elute
- Injector and detector temperatures - 290°C and 320°C, respectively

Standards used for analyses by GC/ECD were prepared from the same stock PCB solutions prepared for analyses by GC/HRMS. Response factors for each chlorine number group (i.e., monochloro-, dichloro-, ...biphenyl isomer) were determined in the same manner as described for the analyses by GC/HRMS. Standard PCB solutions at three different concentrations were chromatographed daily during the analyses in order to monitor the detector response. These daily response factors for each of the 28 PCB compounds determined over several days were averaged. Subsequently, the averaged values for the 3 monochlorobiphenyls were then averaged. This was repeated for each chlorine number group (except the decachlorobiphenyl which has only one isomer), resulting in a total of 10 response factors. As expected and unlike response factors determined by GC/HRMS, the response factors measured by ECD varied in some instances by a factor of three between the three isomers in a given chlorine number group.

PCBs in the samples were quantitated in the same manner as those determined by GC/HRMS. The individual peaks were identified by chlorine number group (i.e., monochloro, dichloro, ...biphenyl) by comparison with the mass chromatograms of the same sample. The area counts of all monochloro-, dichloro-, ...biphenyl isomers were summed, and ratios to the relative molar response factors were calculated.

Results of the analyses of the raw wastes by GC/EDC are given in Table 18.

TABLE 18. CONCENTRATION OF PCBs IN THE RAW WASTE BY GC/ECD
(by Chlorine Isomer Group, mg/mL)

Test #	Chlorine Number Group, mg/mL										
	Cl_1	Cl_2	Cl_3	Cl_4	Cl_5	Cl_6	Cl_7	Cl_8	Cl_9	Cl_{10}	Total
3	0	1.98	5.77	12.2	10.9	28.6	12.0	5.35	0.38	0.045	77.2
4	0	7.68	21.7	44.4	57.1	103	39.5	17.9	1.2	0.120	293
7	0	8.8	25.7	48.3	34.6	91.5	37.6	17.1	1.07	0.172	265
8	0	5.8	17.7	26.9	20.5	61.4	22.3	12.2	0.675	0.157	168
9	0	5.88	16.6	33.0	22.4	75.6	30.9	14.1	0.990	0.140	200
10	0	5.55	15.4	28.8	24.7	68.8	25.8	11.2	0.217	0.083	181

These values are in good agreement with those determined by GC/HRMS, as given in Table 14, with the exception of the sample from Test 3 and the heptachloro chlorine group for all samples. This discrepancy in the heptachlorobiphenyl determinations can be explained by the selection of three heptachloro-PCB isomer standards used in this study. The three which were selected (out of the twenty-four possible isomers) may not be those found in the sample and may have significantly different response factors, which is not the case with the response factors determined by GC/HRMS.

5.4.3 Ion Chromatography

Impinger solutions and water extracts of the probe rinses were analyzed for chloride content as a qualitative indication of the amount of hydrochloric acid collected in the train. Analyses were performed by ion chromatography (IC) by the procedure given below:

Chromatograph: Dionex Model 16 (Dionex Corp., Sunnyvale, CA)
Column: 250 mm anion separator column and an anion suppressor
Eluent: 0.003 M $NaHCO_3$/0.0024 M Na_2CO_3 aqueous solution
Detector: electrical conductivity detector
Regenerant: 1 N aqueous H_2SO_4 solution

For analysis of anions, the eluent and separator column (containing anion resin in the HCO_3^-/CO_3^{2-} form) cause ions in the sample to separate into distinct bands. The retention time of each anion is influenced by the affinity of that ion for the separator column, the eluent used, length of the column, and the flow rate of eluent. The effluent from the separator column is then fed to the suppressor column. Two reactions occur in the suppressor column. The resin (a strong acid resin/H^+ form) removes Na^+ and protonates the HCO_3^-/CO_3^{2-} to H_2CO_3. Thus, anions in the sample exit the suppressor column as acids because the cations are exchanged for H^+ in the suppressor.

Quantitative results are calculated using a linear regression line obtained from a set of calibration standards. An example calculation is given in Appendix B.7.

Several of the samples contained high levels of chloride and required dilutions of 5000:1. The standard curve had a correlation coefficient of 0.9996 over a concentration range of 1 to 30 ppm. The results appear in Table 19.

Table 19. RESULTS OF ION CHROMATOGRAPHIC ANALYSES FOR CHLORIDE ION

Run # - Sample ID*	Concentration from Regression Analysis (µg/mL)	Dilution Factor	Concentration (µg/mL)
3-PR	9.7	50	485
3-IS	10.2	5,000	51,000
4-PR	7.6	50	380
4-IS	15.7	5,000	78,500
5-PR	6.3	0	6.3
5-IS	0	0	0
7-PR	5.7	50	285
7-IS	15.2	5,000	76,000
8-IS	17.7	5,000	88,500
9-IS	20.7	5,000	103,500
10-PR	15.3	10	153
10-IS	15.7	5,000	78,500
10-blank	0	0	0
QC1; H_2O	0	0	0
QC2; Solvent	0	0	0
QC3; H_2O	0	0	0
QC12; H_2O Blank	0	0	0

*PR = Probe Rinse; also includes Impinger Rinse and Line Rinse
IS = Contents of Impingers 1,2,3

5.5 QUALITY ASSURANCE AND QUALITY CONTROL

Two sets of quality assurance (QA) samples were prepared for this study. The first, for determination of TCDFs and TCDDs, was prepared by EPA personnel in TRW's laboratory in RTP. This was discussed in an early section, and the results are given in Appendix G. The second set was prepared by an independent EPA-contractor and submitted to TRW for analysis.

The second set consisted of 12 separate samples. (See Appendix G for a report on the QA effort.) Samples 1 and 2, intended as spikes for Florisil®, were too low in concentration to be analyzed by the prescribed procedure and were therefore analyzed directly and only by GC/ECD. Samples 3 and 4, also intended as spikes for Florisil®, were spiked with TBB, added to a "blank" Florisil® trap, and carried through the prescribed extraction procedure. Samples 5, 6, 9, 11, and 12 were analyzed directly (with any necessary dilution). Samples 7 and 8 were spiked with TBB, added to a "blank" alumina cleanup column and eluted as prescribed for a "real" sample. Sample 10 was intended to simulate a typical sample of waste and was apparently comprised of PCBs in a mineral oil carrier. The mineral oil would have required a cleanup procedure before analysis by GC/HRMS. For this reason, Sample 10 was not analyzed by GC/HRMS.

The final results for Samples 1, 2, 3, 4, 7, and 8 are reported as total ng found and not as concentrations because the original sample volume (unknown to TRW) was processed and finally recovered in 4 mL of solvent for analysis. The remaining samples were analyzed directly as received and are, therefore, reported as concentration values. Table 20 gives the results of analyses of the QA samples by GC/HRMS by chlorine number group and percent recoveries of TBB. Table 21 gives results for the same samples by GC/ECD by chlorine number group. In addition, Table 21 also gives the concentration of PCBs as Aroclor 1254 and/or 1260.

Table 22 gives the actual values of the QA samples as supplied by the independent contractor to EPA (Appendix I). Agreement between the measured (GC/MS results) and expected values is good, within a percent bias of 50 percent.

TABLE 20. CONCENTRATION OF PCBs IN QA SAMPLES BY GC/HRMS

QA #	Cl_1	Cl_2	Cl_3	Cl_4	Cl_5	Cl_6	Cl_7	Cl_8	Cl_9	Cl_{10}	TBB % Recoveries	Units	Sample Type	Sample Volume
1[1]	---	---	---	---	---	---	---	---	---	---	NA[2]	ng	Direct Analysis	0.4 mL
2[1]	---	---	---	---	---	---	---	---	---	---	NA	ng	Direct Analysis	0.4 mL
3	53.1	827	3099	2691	2107	2059	133	ND[3]	ND	ND	105	ng	Flor. Ext.	4 mL
4	53.1	718	3085	2667	2105	2057	131	ND	ND	ND	107	ng	Flor. Ext.	4 mL
5	0.192	3.52	12.76	14.31	13.47	14.16	5.96	0.236	ND	ND	NA	ng/uL	Direct Analysis	As Received
6	0.190	3.50	12.53	15.7	16.5	16.04	5.36	0.15	ND	ND	NA	ng/uL	Direct Analysis	As Received
7	57.5	540	2331	2068	1778	1461	144	ND	ND	ND	97	ng	Alumina C-U[4]	4 mL
8	75.3	679	3032	2538	1917	1871	178	ND	ND	ND	111	ng	Alumina C-U	4 mL
9	20.3	0.11	ND	0.16	0.06	4.95	ND	ND	ND	ND	NA	ng/uL	Direct Analysis	As Received
10[1]	---	---	---	---	---	---	---	---	---	---	NA	ng/uL	Direct Analysis	As Received
11	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	NA	ng/uL	Direct Analysis	As Received
12	0.36	3.64	16.5	19.07	20.2	18.6	5.77	0.26	ND	ND	NA	ng/uL	Direct Analysis	As Received

[1] Not Analyzed; QC 1 and 2 were too low in concentration; QC 10 required cleanup due to apparent presence of mineral oil carrier for PCB.
[2] NA = Not Applicable.
[3] ND = Not Detected.
[4] C-U = Clean-Up.

TABLE 21. CONCENTRATION OF PCBs IN QA SAMPLES BY GC/ECD

QA #	Cl_1	Cl_2	Cl_3	Cl_4	Cl_5	Cl_6	Cl_7	Cl_8	Cl_9	Cl_{10}	Aroclor 1254	Aroclor 1260	Units	Sample Type	Sample Volume
1	ND[1]	12.1	27.7	53.7	46.8	42.7	6.93	0.62	ND	ND	58	48	ng	Direct Analysis	0.4 mL
2	ND	8.88	9.53	45.6	22.7	20.7	5.61	0.97	ND	ND	34.5	57.7	ng	Direct Analysis	0.4 mL
3	ND	656	1708	3388	2292	1822	239	32.6	ND	ND	4054	2346	ng	Flor. Ext.	4 mL
4	ND	632	2032	2448	2312	1832	230	35.3	ND	ND	3837	2328	ng	Flor. Ext.	4 mL
5	ND	9.58	20.1	35.4	24.1	19.2	2.60	0.370	ND	ND	37.3	23.2	ng/μL	Direct Analysis	As Received
6	ND	2.99	14.2	27.3	16.0	14.4	2.13	0.295	ND	ND	28.7	18.9	ng/μL	Direct Analysis	As Received
7	ND	831	1435	2704	2004	1320	212	26.6	ND	ND	3548	2020	ng	Alumina C-U[2]	4 mL
8	ND	752	1276	2508	1632	1680	215	33.2	ND	ND	3042	1763	ng	Alumina C-U	4 mL
9	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ng/μL	Direct Analysis	As Received
10	ND	3.33	2.65	101	134	141	3.57	0.22	ND	ND	399	ND	ng/μL	Direct Analysis	As Received
11	ND	ND	0.001	0.004	0.007	0.010	0.001	0.003	ND	ND	0.013	0.013	ng/μL	Direct Analysis	As Received
12	ND	10.2	16.6	38.7	20.0	21.7	2.58	0.346	ND	ND	34.7	21.4	ng/μL	Direct Analysis	As Received

[1] ND = Not Detected.
[2] C-U = Clean-Up.

TABLE 22. QUALITY ASSURANCE RESULTS

	Expected Value[1]	TRW Value[2] MS	TRW Value[2] ECD	Percent Bias[3] MS	Percent Bias[3] ECD
Florisil®-Spiked Samples (ng)					
1	137.5	NA	191	---	+39
2	137.5	NA	114	---	-17
3	13,750	10,969	10,138	-20	-26
4	13,750	10,816	9,521	-21	-31
7	12,220	8,380	8,533	-31	-30
8	12,220	10,290	8,096	-16	-34
Direct Analysis Samples (ng/μL)					
5	137.5	64.6	111	-53	-19
12	137.5	84.3	110	-39	-20
6	122.2	70.0	77.3	-43	-37
9	6.50	7.26	ND	+11.9	---
11	0	ND	ND	0	0
Waste Oil Sample, (ng/μL)					
10	500	NA	399	---	-20

NA = Not Analyzed

ND = Not Detected

[1] Sum of all PCBs as Aroclor in the sample.

[2] Sum of all PCBs as chlorine isomer group (Cl_1-Cl_{10})

[3] Percent Bias = $\frac{\text{TRW Value - Expected Value}}{\text{Expected Value}}$ X 100

Various quality control measures were implemented during this project in order to maximize the reliability of the results. These measures are discussed in detail in the following paragraphs.

All glassware was initially cleaned by the procedure given in Appendix E. Before any extractions were begun, the "clean" Soxhlet extractors were charged with hexane and allowed to cycle for at least four hours. The hexane was then concentrated in a K-D evaporator and finally reduced to 4 mL in a conical centrifuge tube and analyzed by GC/ECD. This extract had to be free of interferents before a real sample was processed.

After cleaning but before any sample was processed, the glassware was thoroughly rinsed with methanol and hexane. This procedure was checked (repeated Soxhlet extraction with hexane, concentration by K-D to 4 mL, analysis by GC/ECD) and shown to effectively clean the glassware. Each piece of glassware was associated with a given Soxhlet extractor or K-D evaporator by being labeled with a single identifier to ensure that each piece of glassware would always be used as part of a unique set in order to assist in tracing any contamination problem. Each sample was assigned to a given Soxhlet and K-D evaporator and the identifier recorded. Each sample was stored in the centrifuge tube in which it was finally concentrated.

Deuterium-labeled (d_{12}) chrysene was co-injected with each sample as an internal standard for the analyses by GC/HRMS. The response of this internal standard could then be compared with its response when originally co-injected with the 28-PCB compound standard mixture and the TBB. During the analyses by GC/ECD, two standard solutions (one containing all 28 PCB compounds (Table 13) and the other containing only TBB) at three different concentrations were chromatographed daily. The internal standard TBB gave a measure of the extraction efficiency and would also have indicated any losses of sample. Solvent "blanks" and sample "blanks" (i.e., samples from Tests 5-blank and 10-blank) were analyzed to establish background levels of interferents, if present.

5.6 RESULTS OF ANALYSES FOR TCDFs AND TCDDs

Appendix H is the final report from UNL on the analyses for TCDFs and TCDDs. TCDFs were detected in all of the samples of waste and in several samples of stack gas. Results of these analyses are presented in Tables 23 and 24. The analytical method could not distinguish 2,3,7,8-TCDF from the other 37 TCDF isomers*, and so results are presented for total TCDFs. The finding of part per billion levels of TCDFs in the wastes was expected. As seen in Table 24, TCDFs were detected in several stack gas samples. Total concentrations are very small, ranging from <0.3 to <3 ng/m^3 or <0.2 to <2 parts per trillion by weight.

TCDDs, including 2,3,7,8-TCDD, were not detected by UNL in any sample of waste or stack gas taken during the tests. The analytical methodology was such that 2,3,7,8-TCDD could have been unambiguously determined. Detection limits for the wastes ranged from <2 to <22 ng/g or <2 to <22 parts per billion.

Appendix F presents a summary of results of the quality assurance effort on the analyses of TCDFs and TCDDs (Appendix G), and of the analyses of TCDFs and TCDDs (Appendix H).

TABLE 23. CONCENTRATIONS OF TCDFs IN THE WASTE

Test Number	Total TCDFs ng/g
3	42
4	80
7	42
8	25
9	38
10	58

---

*Unambiguous determination of 2,3,7,8-TCDF in the presence of other TCDF isomers cannot yet be made because standards of all 38 isomers are not yet available.

TABLE 24. CONCENTRATIONS OF TCDFs IN STACK GAS SAMPLES

Test Number	Probe Rinse Plus Impingers ng	Florisil® ng	XAD-2® ng	Total ng	Concentration in Stack Gas ng/m^3
3	<1.6[a]	3.9	<0.4	<5.9	<3
3	0.6[b]	c	c	<4.9[d]	<2
4	<0.2	<0.2	c	e	e
7	<0.5	<1.7	c	e	e
8	<0.4	0.4	<0.6	<1.4	<0.7
9	0.0	<0.2	c	e	e
9	c	0.2[b]	c	e	e
10	<0.5	0.0	<1.4	<1.9	<1
10	c	c	<0.1[b]	<0.6[d]	<0.3

[a] A"<" character means TCDFs were not detected. The detection limit was used conservatively to show the maximum value possible.

[b] This analysis was made by GC/HRMS on a capillary column and the others by GC/HRMS on a packed column.

[c] This sample was not analyzed.

[d] These values were derived by combining values from analyses made as in Notes b and c.

[e] Totals are not possible because not all samples were analyzed.

6. DESTRUCTION EFFICIENCIES

The various data required for calculating destruction efficiencies have been given earlier: feed rates in Table 3; sample sizes in Table 4; composition of combustion effluent in Table 5; flow rates of combustion effluent in Table 6; and concentrations of PCBs and chlorobenzenes in the waste and stack gas samples in Tables 14-17; and concentrations of TCDFs in the waste and stack gas samples in Table 23 and 24, respectively. Destruction efficiencies for PCBs and chlorobenzenes are presented by chlorine number group: that is, for monochloro-, dichloro-, ...isomers. They were calculated using the following formula:

$$DE = 100 \times \frac{W_i - W_o}{W_i}$$

Where W_i = mass feed rate of species of interest into the incinerator and W_o = mass emission rate of the species of interest in the stack gas before release to the atmosphere. Now, W_o may be written as F_oC_o, where F_o = the flow rate (dry) of combustion effluent in m^3/hr and C_o = concentration of the species of interest in the combustion effluent. Thus,

$$DE = 100 \times \frac{W_i - F_oC_o}{W_i}$$

An example calculation is given in Appendix B.8. Destruction efficiencies for PCBs and chlorobenzenes are given in Tables 25 and 26, respectively.

Examination of Tables 25 and 26 reveals that destruction efficiencies for PCBs and chlorobenzenes were well above the required minimum of 99.9 percent:

TABLE 25. DESTRUCTION EFFICIENCIES OF PCBs

Test No.	Chlorine No.	W_i kg/hr	C_o ng/m^3	W_o g/hr	DE %
3	1	0.786	<482	<0.031	>99.99607
	2	24.3	<964	<0.062	>99.99974
	3	98.3	<3,854	<0.248	>99.99975
	4	146.	<3,854	<0.248	>99.99983
	5	204.8	<3,372	<0.217	>99.99989
	6	507.8	<5,299	<0.341	>99.99993
	7	341.4	<4,336	<0.279	>99.99992
	8	69.	<1,927	<0.124	>99.99982
	9	ND[a]	ND	--	--
	10	ND	ND	--	--
	Total	1,390.	<24,088	<1.549	>99.99989
4	1	0.909	<500	<0.033	>99.99641
	2	25.2	<1,000	<0.065	>99.99974
	3	98.2	<4,001	<0.261	>99.99973
	4	145.2	<4,001	<0.261	>99.99982
	5	256.	<3,501	<0.228	>99.99991
	6	540.4	<5,502	<0.359	>99.99993
	7	514.6	<4,502	<0.294	>99.99994
	8	102.6	<2,001	<0.130	>99.99987
	9	ND	ND	--	--
	10	ND	ND	--	--
	Total	1,684.	<25,009	<1,631	>99.99990
7	1	ND	--	--	--
	2	25.1	<1,058	<0.068	>99.99972
	3	121.1	<4,231	<0.274	>99.99977
	4	159.5	<4,231	<0.274	>99.99983
	5	218.5	<3,702	<0.239	>99.99989
	6	461.3	<5,818	<0.376	>99.99992
	7	435.8	<4,760	<0.308	>99.99993
	8	98.3	<2,116	<0.137	>99.99986
	9	ND	ND	--	--
	10	ND	ND	--	--
	Total	1,523	<25,918	<1.676	>99.99989

TABLE 25. (CONTINUED)

Test No.	Chlorine No.	W_1 kg/hr	C_o ng/m^3	W_o g/hr	DE %
8	1	ND	--	--	--
	2	25.	<1,024	<0.063	>99.99975
	3	103.5	<4,097	<0.253	>99.99976
	4	115.8	<4,097	<0.253	>99.99978
	5	184.9	<3,585	<0.222	>99.99988
	6	417.9	<5,633	<0.348	>99.99992
	7	378.3	<4,609	<0.285	>99.99992
	8	51.4	<2,048	<0.127	>99.99975
	9	ND	ND	--	--
	10	ND	ND	--	--
	Total	1,281	<25,093	<1.551	>99.99989
9	1	1.28	<516	<0.034	>99.99734
	2	15.	<1,032	<0.068	>99.99954
	3	88.2	<4,128	<0.272	>99.99969
	4	142.2	<4,128	<0.272	>99.99981
	5	245.3	<3,612	<0.238	>99.99990
	6	519.4	<5,675	<0.374	>99.99993
	7	495.7	<4,643	<0.306	>99.99994
	8	99.2	<2,064	<0.136	>99.99986
	9	ND	ND	--	--
	10	ND	ND	--	--
	Total	1,608.	<25,797	<1.702	>99.99989
10	1	ND	--	--	--
	2	21.2	<1,048	<0.068	>99.99968
	3	74.1	<4,194	<0.271	>99.99963
	4	132.1	<4,194	<0.271	>99.99979
	5	230.2	<3,670	<0.237	>99.99990
	6	469.4	<5,766	<0.373	>99.99992
	7	426.2	<4,718	<0.305	>99.99993
	8	102.	<2,097	<0.136	>99.99987
	9	ND	ND	--	--
	10	ND	ND	--	--
	Total	1,454.	<25,687	<1.661	>99.99989

* ND means not detected. When nothing was detected in the waste sample, C_o and W_o are indicated with a "--".

TABLE 26. DESTRUCTION EFFICIENCIES OF CHLOROBENZENES

Test No.	Chlorine No.	Wi kg/hr	Co ng/m^3	Wo g/hr	DE %
3	1	10.6	<482	< 0.031	>99.99971
	2	5.70	<482	< 0.031	>99.99946
	3	182.3	<964	< 0.062	>99.99997
	4	129.1	<964	< 0.062	>99.99995
	5	31.1	<482	< 0.031	>99.99990
	6	53.6	<482	< 0.031	>99.99994
	Total	412.4	<3,854	< 0.248	>99.99994
4	1	4.98	<500	< 0.033	>99.99934
	2	5.74	<500	< 0.033	>99.99943
	3	186.6	<1,000	< 0.065	>99.99996
	4	119.2	<1,000	< 0.065	>99.99994
	5	37.6	< 500	< 0.033	>99.99991
	6	63.2	< 500	< 0.033	>99.99995
	Total	417.2	< 4,000	< 0.261	>99.99994
7	1	0.926	< 529	< 0.034	>99.99631
	2	10.9	< 529	< 0.034	>99.99969
	3	142.9	<1,058	< 0.068	>99.99995
	4	129.1	<1,058	< 0.068	>99.99995
	5	30.1	< 529	< 0.034	>99.99989
	6	28.1	< 529	< 0.034	>99.99988
	Total	342.1	< 4,231	< 0.274	>99.99992
8	1	14.7	< 512	< 0.032	>99.99978
	2	5.03	< 512	< 0.032	>99.99937
	3	173.0	<1,024	< 0.063	>99.99996
	4	93.9	<1,024	< 0.063	>99.99993
	5	21.4	< 512	< 0.032	>99.99985
	6	26.5	< 512	< 0.032	>99.99988
	Total	334.5	< 4,097	< 0.253	>99.99992

TABLE 26. (CONTINUED)

Test No.	Chlorine No.	Wi kg/hr	Co ng/m^3	Wo$_3$ g/m^3	DE %
9	1	5.25	<516	<0.034	>99.99935
	2	4.56	<516	<0.034	>99.99925
	3	165.7	<1,032	<0.068	>99.99996
	4	115.5	<1,032	<0.068	>99.99994
	5	38.3	<516	<0.034	>99.99991
	6	52.5	<516	<0.034	>99.99994
	Total	381.8	<4,128	<0.272	>99.99993
10	1	ND*	--	--	--
	2	6.67	<524	<0.034	>99.99949
	3	104.6	<1,048	<0.068	>99.99994
	4	144.0	<1,048	<0.068	>99.99995
	5	49.0	<524	<0.034	>99.99993
	6	51.2	<524	<0.034	>99.99993
	Total	355.5	<3,670	<0.237	>99.99993

* ND means not detected.

the lowest value for PCBs was >99.9906 percent and the lowest value for chlorobenzenes was >99.996 percent. These high destruction efficiency values* reflect the reasonably large sizes of gas volumes sampled and extremely low detection limits. That none of the sought-for species was detected is also reflective of the fact that the combustion process was very stable and that upsets did not occur during sampling. It was arranged with the Chief Engineer that upset conditions, such as cleaning of burners or changeovers from one tank to another, would be scheduled for times other than when sampling was occurring.

---

*Destruction efficiency values such as these imply that data are known to a very high degree of accuracy (e.g., 10 to 11 significant figures). This, of course, is not the case, as the data are known only to 2 to 4 significant figures.

Results of the analyses for TCDFs performed at UNL were used to calculate destruction efficiencies. These values are presented in Table 27 and are all in excess of 99.9 percent. It is neither possible nor meaningful to calculate destruction efficiencies of TCDDs because these compounds were not detected by UNL in the samples of waste and stack gas taken during these tests.

TABLE 27. DESTRUCTION EFFICIENCIES OF TCDFs

Test Number	W_i g/hr	W_o μg/hr	DE %
3	0.252	<183[a]	>99.93
3[b]	0.252	<151	>99.94
8	0.135	<44	>99.97
10	0.308	<64	>99.98
10[b]	0.308	<20	>99.99
$\bar{x}$[c]	d	d	>99.96
s[c]	d	d	0.02

[a] A "<" character means that TCDFs were not detected. The detection limit was used conservatively showing the maximum value possible.

[b] This sample was analyzed by GC/HRMS and a capillary column and the others by GC/HRMS and a packed column.

[c] $\bar{x}$ and s are mean and standard deviation, respectively.

[d] Not applicable.

7. REFERENCES

1. Wastler, T.A., C.K. Offutt, C.K. Fitzsimmons, and P.E. DesRosiers. Disposal of Organochlorine Wastes by Incineration At Sea. U.S. Environmental Protection Agency, Washington, DC. Report No. EPA-430/9-75-014. July 1975.

2. Clausen, J.F., H.J. Fisher, R.J. Johnson, E.L. Moon, C.C. Shih, R.F. Tobias, and C.A. Zee. At-Sea Incineration of Organochlorine Wastes Onboard the M/T VULCANUS, U.S. Environmental Protection Agency, Research Triangle Park, NC. Report No. EPA-600/2-77-196. (NTIS PB 272-110/AS) September 1977.

3. Ackerman, D.G., H.J. Fisher, R.J. Johnson, R.F. Maddalone, B.J. Matthews, E.L. Moon, K.H. Scheyer, C.C. Shih, and R.F. Tobias. At-Sea Incineration of Herbicide Orange Onboard the M/T VULCANUS. U.S. Environmental Protection Agency, Research Triangle Park, NC. Report No. EPA-600/2-78-086. (NTIS PB 281-690/AS) April 1978.

4. Ackerman, D.G. Destruction Efficiencies for TCDD During At-Sea Incineration of Herbicide Orange. EPA Contract No. 68-02-2660. U.S. Environmental Protection Agency, Research Triangle Park, NC. EPA-600/2-78-087. (NTIS PB 283-642) March 1979.

5. U.S. Environmental Protection Agency. Final Environmental Impact Statement, Designation of a Site in the Gulf of Mexico for Incineration of Chemical Wastes. Washington, DC. July 1976.

6. Paige, S.F., L.B. Baboolal, H.J. Fisher, K.H. Scheyer, A.M. Shaug, R.L. Tan, and C.F. Thorne. Environmental Assessment: At-Sea and Land-Based Incineration of Organochlorine Wastes. U.S. Environmental Protection Agency, Research Triangle Park, NC. Report No. EPA-600/2-78-087. (NTIS PB 283-642) April 1978.

7. Shih, C.C., J.E. Cotter, D. Dean, S.F. Paige, E.P. Pulaski, and C.F. Thorne. Comparative Cost Analysis and Environmental Assessment for Disposal of Organochlorine Wastes. U.S. Environmental Protection Agency, Research Triangle Park, NC. Report No. EPA-600/2-78-190. (NTIS PB 286-095) August 1978.

8. U.S. Department of State and the U.S. Environmental Protection Agency. Final Environmental Impact Statement for the Incineration of Wastes At-Sea Under the 1972 Ocean Dumping Convention. U.S. State Department, Washington, DC. February 1979.

9. U.S. Environmental Protection Agency. Permit No. HQ-81-002. U.S. EPA, Marine Protection Branch, Washington, DC. December 1981.

10. Compaan, H. Monitoring of Combustion Efficiency, Destruction Efficiency and Safety During the Test Incineration of PCB Waste Part 1: Combustion and Destruction - Netherlands Organization for Applied Scientific Research-TNO. Delft, The Netherlands.

11. Metzger, J.F. and D.G. Ackerman. A Summary of Events, Communications, and Technical Data Related to the At-Sea Incineration of PCB-Containing Wastes Onboard the M/T VULCANUS, 20 December 1981 - 4 January 1982. Report to U.S. Environmental Protection Agency, Cincinnati, OH. Contract No. 68-01-3174, Work Assignment No. 82. January 1983.

12. Code of Federal Regulations. U.S. Environmental Protection Agency. Title 40. Parts 220-229. Subchapter H. - Navigable Waters. U.S. Government Printing Office, Washington, DC. Revised as of 1 July 1981.

13. Rutzen, H. Chief Engineer, M/T VULCANUS. Voyage 142 - 2nd PCB Test Burn. Ocean Combustion Service, BV, Rotterdam, The Netherlands, 31 August 1982.

14. Code of Federal Regulations. U.S. Environmental Protection Agency. Title 40, Part 761. Polychlorinated Biphenyls (PCBs) Manufacturing, Processing, Distribution in Commerce and Use Prohibitions. U.S. Government Printing Office, Washington, DC. Revised as of 1 July 1981.

15. Code of Federal Regulations, U.S. Environmental Protection Agency. Title 40, Part 60. Standards of Performance for New Stationary Sources. Appendix A. Reference Methods, U.S. Government Printing Office, Washington, DC. Revised as of 1 July 1981.

16. Ackerman, D.G., J.F. McGaughey, and D.E. Wagoner. Sampling and Analysis Plan for the At-Sea Incineration of PCB Wastes Onboard the M/T VULCANUS. U.S. Environmental Protection Agency, Research Triangle Park, NC. Contract No. 68-02-3174, Work Assignment No. 103. August 1982.

17. Sexton, F.W. and D.E. Lentzen. Audit of the VULCANUS Incineration Ship Prior to the August 1982 PCB Burn, Mobile, Alabama. U.S. Environmental Protection Agency, Research Triangle Park, NC. Contract No. 68-02-3146. Report to EPA-IERL/RTP. February 1983.

18. Beard, J.H., III and J. Schaum. Sampling Methods and Analytical Procedures Manual for PCB Disposal: Interim Report. U.S. Environmental Protection Agency, Office of Solid Waste, Washington, DC. February 1978.

19. Lentzen, D.E., D.E. Wagoner, E.D. Estes, and W.F. Gutknecht. IERL-RTP Procedures Manual: Level 1 Environmental Assessment (Second Edition). U.S. Environmental Protection Agency, Research Triangle Park, NC. Report No. EPA-600/7-78-201. (NTIS PB 293-795) October 1978.

20. American Conference of Governmental Industrial Hygienists. Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes for 1981. Publications Office, ACGIH. Cincinnati, OH 45211.

21. Tindall, W.G. and E. Wininger. J. Chromatography, 196, 109-119 (1980).

APPENDIX A

CHIEF ENGINEER'S VOYAGE REPORT

MT"Vulcanus"
Mobile,Ala. Aug.31,1982

Voyage 142 - 2nd PCB test burn

Before departure of the vessel the accuracy of all thermocouples and the gasanalyser had been checked by the Research Triangel Institute. Results see attached audit summary.

Sunday, Aug. 15, 1982

MT"Vulcanus" left Mobile at 10.00 hrs. Totally loaded are 3031 m^3= 800804 US gal. PCB- containing waste.

Monday, Aug. 16, 1982

At 23.00 hrs. started up both incinerators, 23.30 hrs started preheating.

Tuesday, Aug. 17, 1982

Preheating both incinerators with gasoil. 07.20 hrs arrival combustion area. Temperatures port inc.=650°C, stb inc.=640°C. At 11.00 hrs the plastomatics were adjusted to open at a wall-temperature of 1220°C, see attached EPA- statement. At 11.00 hrs changed burner no. 2 and 5 to waste and started incineration, 11.20 hrs changed burner no. 3 and 4 to waste, at 11.25 hrs changed burner no. 1 and 6 to waste out of tank 1C. At 21.16 hrs heating value tank 1C drops, till 22.40 hrs all burners several times on gasoil, at 22.40 hrs changed over 2 burners to tank 5C. The daily averages: Port inc.=1281°C, 99,98%CE, Stb inc=1290°C, 99,98%CE.

Wednesday, Aug. 18, 1982

Burning out of tank 1C and 5C. At 06.30 hrs to 06.35 hrs cleaned burner no. 1.
The daily averages:
Port inc.=1300°C, 99,99%CE, Stb inc.=1313°C, 99,99%CE.

Thursday, Aug. 19,1982

Burning out of tank 1C and 5C. 06.30 hrs to 06.35 hrs cleaned burner no. 1. 10.05 hrs to 10.10 hrs cleaned burner no. 5.
At 14.00 hrs tank 1C empty,changed all burners to tank 5C. From 14.00 hrs to 14.30 hrs cleaned all burners. At 20.08 hrs changed 2 burners [illegible] tank 2C.
The daily averages:
Port inc.=1304°C, 99,99%CE, Stb inc.=1302°C, 99,99%CE.

Friday, Aug. 20, 1982

Burning out of tank 2C and 5C. 06.05 hrs to 06.17 hrs cleaned burner no. 1 and 5, 08.40 hrs to 08.45 hrs cleaned burner no. 2 and 6.From 20.15 hrs to 20.20 hrs cleaned burner no. 6.
The daily averages:
Port inc.=1304°C, 99,99%CE, Stb inc.=1311°C, 99,98%CE.

Saturday, Aug.21, 1982

At 02.20 hrs tank 5C empty, burning out of tank 4C and 2C. 08.35 all burners on tank 2C. At 12.50 hrs 2 burners out of tank 3C, 4 burners out of tank 2C. From 20.10 hrs to 20.20 hrs cleaned burner no. 5 and 6.
The daily averages:
Port inc.=1305°C, 99,99%CE, Stb inc.=1311°C, 99,99%CE.

Sunday, Aug. 22, 1982

Burning out of tank 2C and 3C. From 07.35 hrs to 07.40 hrs cleaned burner no. 6. At 07.55 hrs Tank 2C empty, all burners out of tank 3C.At 19.00 hrs heating value tank 3C drops, changed over 2 burners to tank 4C, at 20.05 hrs changed 4 burners to tank 4C. From 20.10 hrs to 20.15 hrs cleaned burner no.1.
The daily averages:
Port inc.=1307°C, 99,99%CE, Stb inc.=1309°C, 99,99%CE.

Monday, Aug. 23, 1982

Burning out of tank 3C and 4C. From 02.10 hrs to 02.15 hrs and from 03.15 to 03.20 hrs cleaned burner no. 2. At 13.10 hrs tank 3C empty, changed all burners to tank 4C and transferred approx. 150 m^3 waste to tank 5C. At 18.25 hrs heating value tank 4C drops,

changed 2 burners to tank 50, 1945 hrs 4 burners to tank 50.
The daily averages:
Port inc.=1306°C, 99,99%CE, Stb inc=1309°C, 99,99%CE.

Tuesday, Aug. 24, 1982

Burning out of tank 40 and 50. From 02.15 hrs to 02.25 hrs cleaned burner no. 4 and 5. At 11.35 hrs tank 40 empty, changed all burners to tank 50. At 13.00 hrs changed all burners to tank 2 port and 2 stb.
The daily averages:
Port inc.=1303°C, 99,99%CE, Stb inc.=1303°C, 99,99%CE.

Wednesday, Aug. 25, 1982

Burning out of tank 2 port and 2 stb. From 01.15 hrs to 01.20 hrs cleaned burner no. 5 and from 02.15 hrs to 02.30 hrs cleaned burner no. 3. From 06.15 hrs to 06.30 hrs cleaned burner no. 1 and 2,and from 10.00 hrs to 10.05 hrs cleaned burner no.6. At 13.20 hrs tank 2 port and 2 stb empty, changed over to tank 3 port and 3 stb.
The daily averages:
Port inc.=1306°C, 99,99%CE, Stb inc.=1306°C, 99,99%CE.

Thursday, Aug. 26, 1982

Burning out of tank 3 port and 3 stb. 01.10 hrs to 01.15 hrs cleaned burner no. 6 and from 04.35 hrs to 04.40 hrs cleaned burner no. 1. From 11.55 hrs to 12.00 hrs cleaned burner no. 1. At 16.00 hrs tank 3 port and 3 stb empty, changed over to tank 4 port and 4 stb. From 20.00 hrs to 20.30 hrs cleaned all burners.
The daily averages:
Port inc.=1301°C, 99,99%CE, Stb inc.=1306°C, 99,99%CE.

Friday, Aug. 27, 1982

Burning out of tank 4 port and 4 stb. At 22.00 hrs tank 4 port and 4 stb empty(4 stb 8 m^3 rest), changed over to tank 5 port and 5stb.
The daily averages:
Port inc.=1302°C, 99,99%CE, Stb inc.=1304°C, 99,99%CE.

Saturday, Aug. 28, 1982

Burning out of tank 5 port and 5 stb. From 03.15 hrs to 03.20 hrs cleaned burner no. 2. From 12.00 hrs to 12.05 hrs cleaned burner no. 5. At 15.30 hrs tank 5 port and 5 stb empty(5 stb 8 m^3 rest), changed all burners to tank 5C.
The daily averages:
Port inc.=1303°C, 99,99%CE, Stb inc.=1301°C, 99,99%CE.
From 20.30 hrs to 22.00 hrs tried to install for testing spare probe to gasanalyser in port incinerator. This was not possible because the inside diameter of the steel protection pipe was sightly smaller than the outside diameter of the ceramic tube. In the next port the protection pipe will be machined to a proper inside diameter. Neverless, it is possible to work at the probe insert during operation of the incinerators.

Sunday, Aug. 29, 1982

Burning out of tank 5C. At 04.35 hrs heating value drops, changed burner no. 3 and 4 to gasoil. At 05.20 hrs tank 5C empty, end of incineration. Till 05.40 hrs cooling down the incinerators with all burners on gasoil. At 05.50 hrs stopped both incinerators.
The daily averages:
Port inc.=1290°C, 99,99%CE, Stb inc.=1300°C, 99,99%CE.

Departed combustion area at 05.30 hrs, arrivel Mobile, Ala. on Aug. 31, 09.30 hrs.

16 m^3 restcargo remain on board, tank 4 stb and 5 stb.
Totally incinerated in 282 hours 3015 m^3 PCB- containing waste.
The average waste feed rate was 10,69 m^3/hr.
The gasoil consumption for preheating was 23,5 m^3, the total gasoilconsumption of the incinerators was 42 m^3.
Running hours in the combustion area: ME Port=87 hours, ME Stb= 22 hours.

Both incinerators and the gasanalysor worked during the whole voyage without any disturbances. The two additional fans installed for the combustion room compensated the ab. 15°C higher outside temperatures compared to the first PCB- burn in December 1981. The temperatures inside the combustion room averaged ab. 55°C at the contoll desc and about 75°C in the other parts of the combustion room.
The strong vibrationes accured at the burners during the first PCB- burn were reduced to a minimum due to increasing the atomiser air- flow by machining the atomizer caps on the burners to a larger inside diameter.

H. Rutzen
....
Helmut Rutzen, chief eng.

MTS "VULCANUS"
Vulcanus Shipping Co. Pte. l
S I N G A P O R E

Tank No. 6 BB CBM = 112	**Tank No. 5 BB** CBM = 117 116 m³ S.G. 1,28 145 to	**Tank No. 4 BB** CBM = 150 145 m³ S.G. 1,18 171,1 to	**Tank No. 3 BB** CBM = 116 113 m³ S.G. 1,28 137,9to	**Tank No. 2 BB** CBM = 128 126 m³ S.G. 1,25 157,5 to	
Tank No. 5 Centre CBM = 415 315 CBM S.G.1,20 378 to	**Tank No. 4 Centre** CBM = 425 402 CBM S.G. 1,24 490,5 to	**Tank No. 3 Centre** CBM = 398 380 CBM S.G. 1,15 437,0 to	**Tank No. 2 Centre** CBM = 562 566 CBM S.G. 1,10 622,6 to		**Tank No. 1** CBM = 444 380 CBM S.G. 1,20 456,0 to
Tank No. 6 STB CBM = 112	**Tank No. 5 STB** CBM = 117 116 CBM S.G. 1,25 145,0 to	**Tank No. 4 STB** CBM = 150 144 CBM S.G. 1,10 169,9 to	**Tank No. 3 STB** CBM = 116 113 CBM S.G. 1,22 137,9 to	**Tank No. 2 STB** CBM = 128 125 CBM S.G. 1,25 156,3 to	

Shore figures:

PCD&S = 793.990 gallons
Diesel = 4.110 gallons

Total = 798.100 gallons

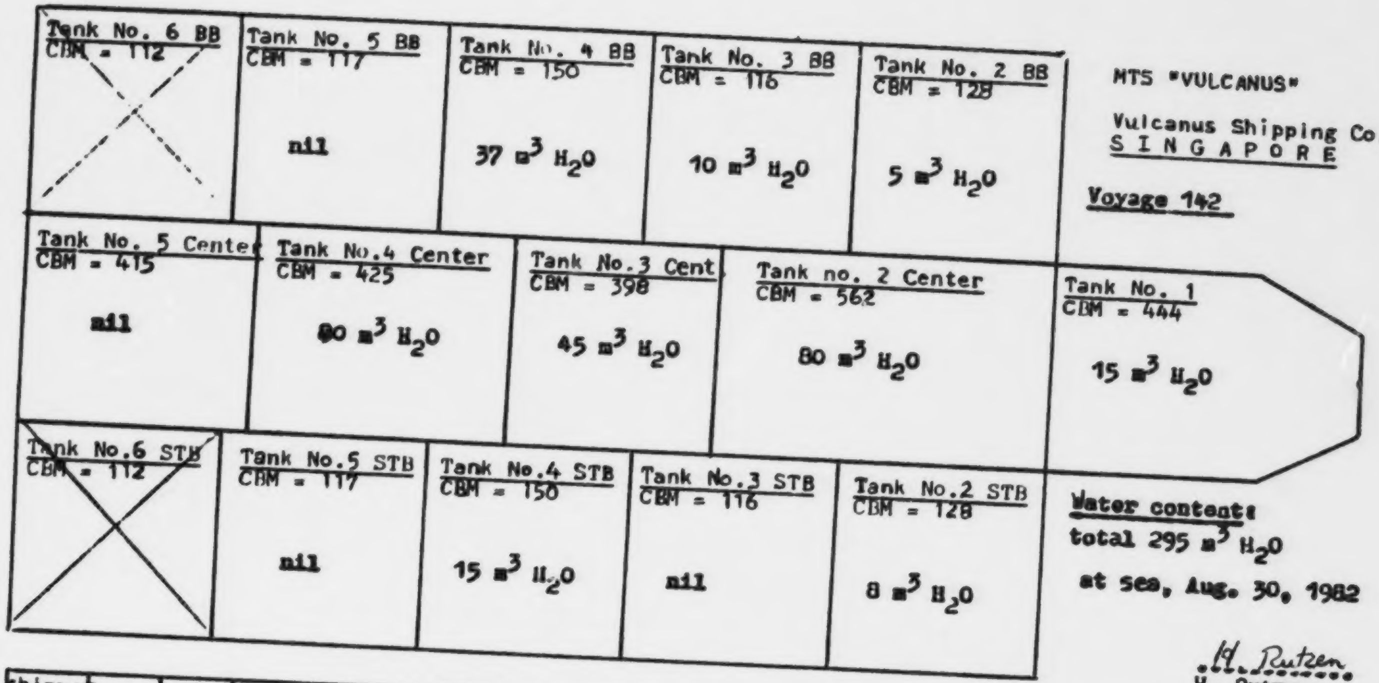
corr. 18.08 vom Kapitän 810 804 ~ 3034 m³

Shipper	1	2 BB	2 CTR	2 STB	3BB	3CTR	3 STB	4BB	4CTR	4STB	5BB	5CTR	5STB	6BB	6STB	TOTAL CBM
	300	126	566	125	113	380	113	145	402	144	116	315	116	XX	XX	~~3.041,0 m³~~
																003.347.1 gallons
TOT CBM																

MTS "VULCANUS"

Vulcanus Shipping Co.
SINGAPORE

Voyage 142



Tank No. 6 BB
CBM = 112

Tank No. 5 BB
CBM = 117
nil

Tank No. 4 BB
CBM = 150
37 m^3 H_2O

Tank No. 3 BB
CBM = 116
10 m^3 H_2O

Tank No. 2 BB
CBM = 128
5 m^3 H_2O

Tank No. 5 Center
CBM = 415
nil

Tank No.4 Center
CBM = 425
80 m^3 H_2O

Tank No.3 Cent
CBM = 398
45 m^3 H_2O

Tank no. 2 Center
CBM = 562
80 m^3 H_2O

Tank No. 1
CBM = 444
15 m^3 H_2O

Tank No.6 STB
CBM = 112

Tank No.5 STB
CBM = 117
nil

Tank No.4 STB
CBM = 150
15 m^3 H_2O

Tank No.3 STB
CBM = 116
nil

Tank No.2 STB
CBM = 128
8 m^3 H_2O

Water content:
total 295 m^3 H_2O
at sea, Aug. 30, 1982

H. Rutzen
H. Rutzen
chief eng.

Shipper	1	2 BB	2 CTR	2 STB	3BB	3CTR	3STB	4BB	4CTR	4STB	5 BB	5CTR	5STB	6BB	6STB	TOTAL CBM
total CBM																

11/78

MTS "VULCANUS"

Vulcanus Shipping Co.
SINGAPORE

End of voyage 142

Tank No. 6 BB CBM = 112	Tank No. 5 BB CBM = 117 empty	Tank No. 4 BB CBM = 150 empty	Tank No. 3 BB CBM = 116 empty	Tank No. 2 BB CBM = 128 empty
Tank No. 5 Center CBM = 415 empty	Tank No.4 Center CBM = 425 empty	Tank No.3 Cent. CBM = 398 empty	Tank no. 2 Center CBM = 562 empty	Tank No. 1 CBM = 444 empty
Tank No.6 STB CBM = 112	Tank No.5 STB CBM = 117 8 m³	Tank No.4 STB CBM = 150 8 m³	Tank No.3 STB CBM = 116 empty	Tank No.2 STB CBM = 128 empty

at sea, 29. Aug., 1982

H Rutzen
....
H. Rutzen
chief eng.

Shipper	1	2 BB	2 CTR	2 STB	3BB	3CTR	3STB	4BB	4CTR	4STB	5 BB	5CTR	5STB	6BB	6STB	TOTAL CBM
total CBM																

11/78

Aug. 23, 1982

To Whom It May Concern:

I removed the seals from the Plastomatics on board the M/T VULCANUS. My experts had checked the wall temperature thermocouples and found that they read correctly. However the plastomatics did not agree with them. The plastomatics would cut off the flow of PCB waste if wall temperature fell below 1270 dgs C. The Permit issued by E.P.A. only requires that the feed be cut if wall temperature falls below 1200 dgs C. There fore I set the Plastomatics to cut off when the wall temperatures drop to 1220 dgs C.

Merrill Jackson
E.P.A. Official
Observer for the
2nd PCB Research Burn.

AUDIT SUMMARY - PRELIMINARY*

Helmut Rutzen
MT "VULCANUS"
c/o Page & Jones
52 N. Jackson St. Mobile, AL
30001
(205) 432-1646

THERMOCOUPLES

		Average % Difference (Audit to Standard)
Port Side - Combustion		
Black Box Meter		5.2%
Combustion Room Meter		4.0%
- Plastomatic		4.7% (Low)
Starboard - Combustion		
Black Box Meter		5.3%
Combustion Meter		5.3%
Plastomatic	→	20.2% (High)

SIEMANS ANALYZERS

O_2 - Starboard Incinerator Probe		7.4% Diff.
CO_2- " " "		8.0% Diff.
CO - " " "	→	38.3% (Low)

→ Leak found in starboard incinerator sample probe. 4th engineer disassembled sample probe, ground seal and reassembled. No leak afterwards. Also tested port side incinerator sample probe and did not detect leak.

→ CO analyzer tends to drift. A good operation is to calibrate daily and if you have a drifty analyzer, check more often.

Fred Sexton
(919) 541-6730

APPENDIX B

EXAMPLE CALCULATIONS

APPENDIX B. EXAMPLE CALCULATIONS

B.1 CALCULATION OF FEED RATE

Data presented in Table 2 showed that the total cargo weighed 3,523 mt. In Appendix A, the Chief Engineer showed that 16 m^3 of water was returned to port. Assuming that the specific gravity of the returned water was 1.00, then 16 mt of water were returned, and 3,507 mt were burned in 282 hours. The average feed rate for the entire cargo was thus 12.43 mt/hr (6.22 mt/hr/incinerator). Given an average specific gravity of 1.16, corresponding volumetric feed rates were 10.7 m^3/hr (5.35 m^3/hr/incinerator).

Waste feed rates were not measured during each test because motions of the ship would have made such measurements too inaccurate. Waste feed rates for each test were calculated as described in this paragraph. The M/T VULCANUS typically burns waste as rapidly as possible as long as an upper limit on wall temperature (about 1300°C) is not exceeded. Feed rate is thus inversely proportional to heat content: the higher the heat content, the lower the feed rate, and vice versa. Therefore, the feed rate for each test was calculated by multiplying the overall waste feed rate (6.22 mt/hr/incinerator) by the ratio of the average heat content (9,858 Btu/lb, from Table 2) to the heat content measured on the sample of waste from the test of interest (values are presented in Tables 3 and 12). For Test 3, the measured heat content was 10,146 Btu/lb. Thus, the calculated feed rate per incinerator during Test 3 was

$$(6.22 \text{ mt/hr} \times 9{,}858 \text{ Btu/lb})/10{,}150 \text{ Btu/hr} = 6.041 \text{ mt/hr}$$

B.2 CALCULATION OF VOLUME OF GAS SAMPLED

Reference 15 provides the following relationship for calculating the corrected, standard volume of gas (Vm, std) sampled with a train of the type used in this project:

$$Vm\ (std) = Vm.Y.\ \frac{Ts}{Tm} \cdot \frac{Pb + \Delta H/13.6}{Ps}$$

where Vm = volume of gas measured by the dry gas meter, Y = meter box correction factor, Ts = standard temperature (528°R, 20°C), Tm = average absolute temperature of dry gas meter (460 + average temperature), Pb = ambient pressure, Ps = standard pressure (29.92 in Hg), ΔH = average pressure differential across the orifice meter. During Test 3, the following data were taken: Vm = 79.414 ft^3, Y = 0.9961, Tm = 113°F, Pb = 29.99 in Hg, and ΔH = 1.46 in Hg. Therefore,

$$Vm\ (std) = 79.414 \times 0.9961 \times \frac{528}{573} \cdot \frac{29.99 + 1.46/13.6}{29.92}$$

$$= 73.294\ ft^3 \times 0.02832\ m^3/ft^3 = 2.0757\ m^3$$

B.3 CALCULATION OF COMPOSITION OF COMBUSTION EFFLUENT

B.3.1 Volumes of Components Emitted Per Metric Ton of Waste

The following definitions are used:

C = Weight fraction of carbon in the waste

Cl = Weight fraction of chlorine in the waste

O = Weight fraction of oxygen in the waste

H = Weight fraction of hydrogen in the waste

S = Weight fraction of sulfur in the waste

N = Weight fraction of nitrogen in the waste

mt = Metric ton

EA = Excess air

- $V(CO_2) = (C/12.011) \times 10^6$ g/mt $\times$ 0.02406 m^3/mole at 20°C
- $V(HCl) = (Cl/35.453) \times 10^6$ g/mt $\times$ 0.02406 m^3/mole at 20°C
- $V(O_2) = V(CO_2) \times \%O_2/\%CO_2$

- $V(N_2) = \left[\frac{C}{12.011} + \frac{1}{4} \left(\frac{H}{1.008} - \frac{Cl}{35.453} \right) - \frac{O}{32} + \frac{S}{32.065} + \frac{N}{2x28.019} \right] \times$

  10^6 g/mt x 0.02406 m^3/mole x (0.7902/0.2095)(1 + EA) m^3/mt at 20°C

- $V(H_2$, combustion)

  = (1/2)(H/1.008 - Cl/35.453) x 10^6 g/mt x 0.02406 m^3/mole at 20°C

- $V(H_2O$, air)

  = $(V(N_2)/0.7902)\ (P_{H_2O}/760\ \text{mm})$

Relative humidities were not measured. A value of 80% was chosen. P_{H_2O} was thus taken as 80% of the saturation pressure at the ambient temperature of the test.

- $V(SO_2)$ = (S/32.065) x 10^6 g/mt x 0.02406 m^3/mole at 20°C

Organically bound nitrogen was assumed to be converted to N_2 and NO_2 on a 50:50 mole basis. So,

- $V(N_2)$ = (N/(2 x 28.019)) x 10^6 g/mt x 0.02406 m^3/mole at 20°C
- $V(NO_2)$ = (N/(2 x 46.007)) x 10^6 g/mt x 0.02406 m^3/mole at 20°C

Note that conversion of half of the originally bound nitrogen to NO_2 consumes air. This accounts for the appearance of a factor involving N in the equation for $V(N_2)$. It was assumed that one-half of organically bound nitrogen was converted to NO_2 and one-half to N_2.

B.3.2 Volumetric Rates of Emissions

Using data from Test 3 (feed rate = 6.041 mt/hr, C = 0.4871, Cl = 0.4312, O = 0.0271, H = 0.0521, S = 0.0004, N = 0.0006, % O_2 = 10.07, % CO_2 = 9.17, and excess air = 93.32%), the following volumetric flow rates were caluclated (in m^3/hr/incinerator at 20°C):

- $V(CO_2)$ = 5,725
- $V(HCl)$ = 1,783
- $V(O_2)$ = 6,287
- $V(N_2)$ = 50,487

- $V(H_2O, \text{comb.}) = 2,734$
- $V(H_2O, \text{air}) = 2,278$
- $V(SO_2) = 2$
- $V(N_2) = 2$
- $V(NO_2) = 1$
- V_T, wet = 69,300
- V_T, dry = 64,288

Therefore, on a wet basis

- % HCl = 100 x 1,783/69,300 = 2.6%
- % H_2O = 100 x 5,012/69,300 = 7.2%
- % N_2 = 100 x 50,487/69,300 = 72.8%

Concentrations of O_2 and CO_2 and excess air used in these calculations were averages over the durations of the tests rather than the daily averages as reported in Table 5.

B.4 CALCULATION OF EXCESS AIR

Excess air values were calculated using the following equation (EPA Method 3, Reference 15):

$$EA = 100 \times \frac{\% O_2 - 0.5\% CO}{0.264 (\% N_2) - \% O_2 - 0.5\% CO}$$

A value of 79.02% was taken for % N_2. This is the sum of the percentages of the nitrogen (78.09%) and argon (0.93%) in the atmosphere. Taking data from Test 3 (% O_2 = 9.9 and % CO = 0.0008), excess air was calculated to be 90%.

B.5 CALCULATION OF COMBUSTION EFFICIENCY

Combustion efficiency is calculated using the following relationship (8,9):

$$CE = 100 \times (\% CO_2 - \% CO)/\% CO_2$$

Using data from Test 3 (% CO^2 = 9.9 and % CO = 0.0008), combustion efficiency is calculated to be 99.99%.

B.6 EXAMPLE CALCULATION FOR THE QUANTITATION OF PCB RAW WASTE, TEST 4 FOR Cl_1 ISOMERS

Relative Molar Response Factors (RMRF) were determined for each chlorine isomer group (i.e., mono, di, tri...chloro PCBs) relative to Tribromobiphenyl (TBB). The low mass ion (LMI) for the TBB (m/z 388) was monitored along with the LMIs for each chloro group in a given sample. The quantitative calculations were then performed in the following way.

$$\frac{(\text{Total area counts for LMI of } Cl_1 \text{ isomers})}{(\text{Area Counts per } \rho \text{ mole TBB}) \times (\text{RMRF})} \times \text{molecular weight } Cl_1 \text{ isomer} =$$

$$\mu g/\mu L \text{ (or mg/mL)}$$

$$\frac{575}{165.2 \times 3.37} \times 188 = 194\ \mu g/\mu L \text{ (or 0.194 mg/mL)}$$

B.7 EXAMPLE OF CALCULATION OF CHLORIDE ION FROM ION CHROMATOGRAPHIC ANALYSES

Quantitative results are calculated using a linear regression line obtained from a set of calibration standards. An example calculation is given below.

Standard Solution No.	Concentration	Peak Height
1	C_{s1}	P_{s1}
2	C_{s2}	P_{s2}
3	C_{s3}	P_{s3}

A linear regression analysis of these data yields the standard calibration equation

$$P_{s,i} = (\text{Slope}) \times (C_{s,i}) + (\text{Intercept}).$$

The peak height for an unknown, P_u, is measured as well as that of a blank, P_b. Concentrations $C_{u,\text{ measured}}$ and C_b are calculated using the standard calibration equation, and $C_{u,\text{ corrected}}$ is calculated as

$$C_{u,\text{ corrected}} = C_{u,\text{ measured}} - C_b.$$

B.8 CALCULATION OF DESTRUCTION EFFICIENCIES

Test 3 will be used as an example throughout this section.

B.8.1 Feed Rates of PCBs and Chlorobenzenes

The waste burned during Test 3 was fed at a rate of 6.041 mt per hour per incinerator and had 0.16 mg/mL of monochlorobiphenyl (MCB) and a specific gravity of 1.23 g/mL. The feed rate of MCB was:

$$W_i = 0.16 \frac{\text{mg}}{\text{mL}} \times 10^{-3} \frac{\text{g}}{\text{mg}} \times \frac{1 \text{ mL}}{1.23 \text{ g}} \times 10^{3} \frac{\text{kg}}{\text{mt}} \times 6.041 \frac{\text{mt}}{\text{hr}} = 0.786 \frac{\text{kg}}{\text{hr}}$$

B.8.2 Emission Concentrations Measured

It was noted in Chapter 5 that the analytical scheme was intended to determine PCBs and chlorobenzenes by chlorine number (i.e., monochloro-dichloro-, etc.). Therefore, the number of monochlorobiphenyl isomers and the concentration of each were determined in the samples of waste and stack gas. The same process was followed through decachlorobiphenyl and mono- through hexachlorobenzene.

A total of 209 PCBs is possible, and they are distributed* as follows:

- Mono - 3
- Di - 12
- Tri - 24
- Tetra- 42
- Penta- 46
- Hexa - 42
- Hepta - 24
- Octa - 12
- Nona - 3
- Deca - 1

A total of 12 chlorobenzenes is possible, and they are distributed as follows:

- Mono - 1
- Di - 3
- Tri - 3
- Tetra - 3
- Penta - 1
- Hexa - 1

Because of the way PCBs and Askarels® (mixtures of PCBs and chlorobenzenes) are manufactured, there is no reason to expect and it is not found that all of the possible individual isomers will be present in an Aroclor® or Askarel®. Analyses of the wastes (Table B-1) verified this expectation.

---

*Cairns, T. and E.E. Siegmund. PCBs - Regulatory History and Analytical Problems. Analytical Chemistry, 53, 1183A (1981).

TABLE B-1. NUMBERS OF ISOMERS FOUND IN SAMPLES
OF WASTE BY CHLORINE NUMBER

Chlorine Number	Test Number					
	3	4	7	8	9	10
PCBs						
1	1	1	0	0	1	0
2	2	2	2	2	2	2
3	8	8	8	8	8	8
4	8	8	8	8	8	8
5	7	7	7	7	7	7
6	11	11	11	11	11	11
7	9	9	9	9	9	9
8	4	4	4	4	4	4
9	0	0	0	0	0	0
10	0	0	0	0	0	0
Total	50	50	49	49	50	49
Chlorobenzenes						
1	1	1	1	1	1	0
2	1	1	1	1	1	1
3	2	2	2	2	2	2
4	2	2	2	2	2	2
5	1	1	1	1	1	1
6	1	1	1	1	1	1
Total	8	8	8	8	8	7

No PCB or chlorobenzene compound was detected in any stack gas sample. This does not mean that emissions of these compounds were zero. Emissions of these compounds are probably greater than zero and were found to be less than the detection limit. However, it is common and conservative practice to use the detection limit as the estimate of emissions and to use the "less than" character (<) to indicate that the compound thus identified was not detected.

As described in Section 5, the detection limit for any of the PCBs or chlorobenzenes in the probe rinse samples was 100 picograms (pg = 10^{-12} g) per µL injected, and in the combined samples (extracts of Florisil®, XAD-2®, and impingers) was 25 pg/µL. The overall detection limit was 125 pg/µL. Recalling that each sample or extract, as appropriate, was split into two equal parts (one-half for analyses for PCBs and chlorobenzenes and the other half for analyses for TCDFs and TCDDs) and that the TRW half-sample was concentrated to 4 mL before being analyzed, the detection limit for any PCB or chlorobenzene compound was taken as 1.00 μg per sample. Consequently, emissions of any PCB or chlorobenzene compound were less than 1.00 μg per sample.

Because analytical results were grouped by chlorine number and because there could be more than one isomer per chlorine number, the detection limit for a sample was multiplied by the number of isomers per chlorine number present in the waste. For example, only one monochlorobiphenyl isomer was found in any waste sample. Because this compound was not detected in the stack gas samples, emission of monochlorobiphenyl are taken as <1.00 μg per sample. In the case of trichlorobenzene, two isomers were detected in the waste but not in the stack gas samples. Thus, emissions of trichlorobenzenes are taken as <2.00 μg per sample.

Based on the foregoing discussion, the maximum concentration of monochlorobiphenyl that could have been emitted but still be undetected during Test 3 was:

$$C_o = <125 \times \frac{10^{-12}\text{g}}{\mu\text{L}} \times \frac{4{,}000\ \mu\text{L}}{\text{half-sample}} \times 2\ \frac{\text{half-samples}}{\text{sample}} \times 1\ \text{isomer} \times \frac{1\ \text{sample}}{2.0757\ \text{m}^3}$$

$$= <4.82 \times 10^{-7}\ \text{g/m}^3\text{, and}$$

$$W_o = C_oF_o = (<0.482\ \mu\text{g/m}^3)(64{,}288\ \text{m}^3\text{/hr}) = 0.0310\ \text{g/hr}$$

B.8.4 Destruction Efficiencies

The destruction efficiency for MCB was calculated thusly:

$$DE = 100 \times \frac{W_i - W_o}{W_i}$$

Where W_i is the mass feed rate of the sought-for species and W_o is the mass emission rate of the sought-for species measured in the sample. From Appendices B.8.1 and B.8.2,

$$DE = 100 \times (786\ \text{g/hr} - <0.031\ \text{g/hr})/786\ \text{g/hr}$$

$$= >99.99607$$

APPENDIX C

SELECTED PORTIONS OF EPA RESEARCH PERMIT HQ-81-002

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OFFICE OF
WATER

Mr. Frank Krohn
Chemical Waste Management, Inc.
3003 Butterfield Road
Oak Brook, Illinois 60521

Dear Mr. Krohn:

This letter sets forth our understanding of the meaning of several permit provisions in accordance with discussions between Chemical Waste Management, Inc., Ocean Combustion Service, Inc., and the U.S. Environmental Protection Agency representatives during the recent inspection of the Vulcanus and the review of the planned implementation of Research Permit HQ-81-002.

1. General Conditions: 14 d. (page 5)

   The sample of "material incinerated" would be emissions from the incineration.

2. Special Conditions: 3. Amount of Material, part c

   Destruction efficiencies for PCB's, PCDF, and total chlorinated organics may be determined on-shore.

3. Special Conditions: 7. Monitoring Requirements, part a

   In the event of instrument failure with no apparent loss of combustion efficiency, the EPA observer may allow incineration to proceed for approximately 24 hours if the remaining monitoring equipment supports a reasonable conclusion that the combustion efficiency requirements are met. The following table suggests the combinations of monitoring instrumentation which we feel are sufficient during this "breakdown" period.

WORKING COMBINATIONS OF MONITORING INSTRUMENTATION

Measured Parameter	1	2	3[a,b]	4[c]	5[b]	6[a]
CO	X	X	X		X	
CO_2	X	X		X		
O_2	X		X	X		X
Wall Temperature	X	X	X	X	X	X

---

a And $O_2 > 3\%$
b And $CO < 100$ parts per million
c And $O_2 > 3\%$

4. Special Conditions: 9. Research Plan part b

   In light of the change in the permit to incorporate destruction efficiency successive burns shall be contingent on successful demonstration of a destruction efficiency of 99.9% for PCB's and chlorinated organics in the previous burn as well as the combustion efficiency requirement.

5. Special Conditions: The Reports and Correspondence

   This section should have been numbered item 11, not item 10.

6. Appendix A: Characteristics of the Materials to be Incinerated

   This section describes generally the characteristics of the waste material. More detailed information contained in the manifests for each truckload of material is also required.

7. Appendix B: Safety Plan 2. Potential Hazards

   The Threshold Limit Value (TLV) of 0.05 micrograms/m^3 in the permit is an error. This section requires that best practice be applied to the operations of the incinerator so as not to allow an increase from background ambient PCB levels. Corrective action must be taken when levels are increasing, but in no case shall levels be permitted to exceed 5 micrograms/m^3.

I wish to thank you for your cooperation during the review and inspection.

Sincerely yours,

Bruce R. Barrett

Bruce R. Barrett
Acting Assistant Administrator
for Water

cc: Donald Obernacker, ERL-Cinn.
David Sanchez, ORD-RTP

Special Conditions

1. Permit term - this Permit shall be in effect 6 months from the effective date of the permit.

2. Description of Material

a. The waste to be transported for incineration is a mixture of polychlorinated biphenyls and rinsate which shall be diesel fuel. The PCB waste shall not differ significantly from that set forth in Appendix A.

b. The character of the material being incinerated shall not be altered in its content from the proportions listed in Appendix A or by the addition of wastes from sources other than those identified above.

c. The specific source and amount from each source of the waste materials to be incinerated in each burn must be reported to the Assistant Administrator for Water 10 working days prior to loading the vessel with that specific batch of waste.

3. Amount of Material -

a. The Permittees are authorized to transport and incinerate material described in Special Condition No. 2 in an amount not in excess of 3.6 million gallons.

b. The Permittees shall submit reports of actual volumes incinerated within 10 days after each incineration cruise.

c. Destruction efficiency for PCB's shall be calculated. Within the detection limits of available equipment, the destruction efficiency also will be calculated for the PCDF's. These values shall be reported within 45 days of the completion of each cruise.

4. Transportation and Barging Activities -

a. The port of departure for the incineration of the material described herein shall be Mobile, Alabama.

b. During loading operations, transport, and incineration at sea, there shall be no loss of material to any waterway or ocean waters.

c. Reports, approval forms, copies of any survey reports, and copies of this permit and safety plan shall be kept on the M/T VULCANUS.

5. Disposal Site - Transportation for the purpose of this Permit shall terminate at, and all waste incineration shall be confined to the area described below:

Gulf Incineration Site

Latitude	Longitude
26° 20'00"N	93° 20'00"W
26° 20'00"N	94° 00'00"W
27° 00'00"N	93° 20'00"W
27° 00'00"N	94° 00'00"W

The Permittees shall navigate around, by a radius of at least 15 nautical miles, the reefs found at the following coordinates:

West Flower Gardens:

93°48'W 27°15'N

East Flower Gardens:

27°55'N 93°36'W

The permittees shall also navigate around, by a radius of at least 5 nautical miles, the reefs found at the following coordinates:

	Claypile Bank	
28°20'N		94°09'W
	Stetson Bank	
28°10'N		94°18'W

6. Method of Disposal

a. The M/T VULCANUS shall be used for incineration at sea of the material described above.

b. During start-up, PCB's shall not be fed into the incinerators until a wall temperature of 1200°C has been reached in the furnace, and only one burner at a time may be changed over to the waste.

c. During tank changeover, prior to each subsequent tank depletion, the ship shall be underway and oriented in such a direction as to minimize plume impingement should incinerator flame be extinguished. At least 15 minutes before tank depletion, pumping shall be switched so that 2 burners of each incinerator shall be fed from a full tank, with the remaining burner used to deplete the material in the emptied tank.

d. The speed and direction of the M/T VULCANUS during waste incineration shall be controlled in such a manner to prevent incinerator plume contact with the ship.

e. The incinerator wall temperature shall be greater than 1200°C and the mean residence time shall be greater than 0.7 second at that temperature.

f. An automatic shut-off device shall be in operation on both furnaces, set to turn off the flow of PCB waste if the wall temperature falls below 1200°C; or if the flame is extinguished.

g. The combustion efficiency of the incinerator during the incineration will be at least 99.9 per cent complete. If the combustion efficiency level falls below 99.9 per cent, the waste feed on the M/T VULCANUS shall be shut down immediately until corrective measures which assure 99.95±0.05 per cent combustion efficiency are applied.

h. Tank washings and pump-room bilges contaminated with wastes shall be incinerated at sea in accordance with these regulations or discharged to port facilities.

i. Residues remaining in the incinerator shall not be dumped at sea.

j. There shall be no black smoke nor extension of the flame above the plane of the stack.

7. Monitoring Requirements -

a. Continuous monitoring of CO, CO_2, O_2, wall temperature, and combustion efficiency, shall be in effect during the entire operation.

b. The operational controls and monitoring panels shall be manned at all times by a responsible individual to insure the incinerators are operating at the 99.95±0.05% minimum combustion efficiency.

c. A device for addition of ammonia to make a visible plume shall be installed and operable.

d. An automatic sealed monitoring device ("black box") will be installed to record CO, CO_2 and O_2 and wall temperatures and a camera mounted so as to photograph the control panel every 15 minutes.

e. An hourly manual log will also be kept, including, but not limited to:

(1) Time, date;

(2) "Black box" wall temperature and CO, CO_2 and O_2 and calculated combustion efficiency;

(3) Controller temperature reading;

(4) Waste feed rates, and tank from which waste is taken;

(5) Wind speed and direction;

(6) Vessel position by appropriate navigational means; vessel course and speed.

f. The manual log will also be kept during tank changeover.

g. Calibration of instruments measuring CO, CO_2, O_2 shall be made with standard mixtures brought on board the M/T VULCANUS for that purpose.

APPENDIX A

CHARACTERISTICS OF THE MATERIAL TO BE INCINERATED

1. Physical description before incineration

The physical properties of the material to be incinerated are as follows:

Transportation temperature:	Ambient	
Specific gravity of the liquid at 20°C:	0.9-1.5	
Boiling point range:	65-390°C	
Pour point:	greater than or equal to 10°C	
Vapor pressure:	25°C	0.006 Torr to 75 Torr
	150°C	4.3 Torr to 200 Torr
	200°C	29.0 Torr to 450 Torr
Saybolt Viscosity:	100°F	1800-2500
	130°F	260-340
	200°F	44-48
Coefficient of thermal expansion:	0.00066 cc/cc/°C	
Solubility in water:	0.09 mg/L	
BTU/lb:	5,400 - 12,000	
Molecular weight:	180-500	

2. General Chemical description before incineration

Trichlorobenzene, kerosene, pump oils, PCB's, and other organic components. Trace metal contaminants measured: at the lower detection limit of 1 ppm: Cu, Fe, Al, Zn; and others at the lower detection limit of 5 ppm: Cr, Pb, Ni, Mn and Ag. Sulphur may be present up to 250 ppm.

3. After incineration

CO_2, H_2O, and HCL as gases and trace metal particulates.

4. The quantity of material to be incinerated may be up to 3.6 million gallons.

3. CRITERIA FOR TERMINATION OF A BURN

Due to the highly toxic nature of the PCDF contaminants possibly present in the PCB wastes and/or in the stack gases, the TNO safety officer shall, in consultation with the cognizant EPA representative and the ship's master, retain the authority to terminate and/or initiate incineration. The criteria that will be used to measure safe shipboard operation are discussed in the following sections. These criteria will only be used as guidelines. It should be recognized that, in addition to the TNO safety officer, authority to terminate any individual incineration burn shall also rest with any one of the following personnel: EPA designate and the master of the M/T VULCANUS.

3.1 Plume impingement

The plume arising from the incinerator stacks will be injected with ammonia as required to make it visible as necessary. Incineration of PCB wastes will be terminated and shipboard personnel will be withdrawn to a safe area if at any time during the test the plume is observed to remain on the deck of the M/T VULCANUS even after corrective measures have been attempted. The plume must be visible also at night, and the position of the plume relative to the ship must be known at all times on the bridge.

3.2 PCB waste spills

Incineration will be terminated if a spill occurs on board the M/T VULCANUS and cannot be readily contained or cleaned up.

3.3 Combustion efficiency

The CO and CO_2 levels determined at or near the exit plane will be used as an indication of overall combustion efficiency using the following equation:

$$\%\ \text{Combustion Efficiency} = \frac{CO_2\ \text{concentration} - CO\ \text{conc.}}{CO_2\ \text{concentration}} \times 100$$

Combustion efficiencies in excess of 99.9 per cent are deemed necessary as an indication that high destruction efficiencies for the PCB waste constituents may be anticipated. The combustion efficiency corresponds at 99.9% to approximately 100 ppm CO in the stack gas. Large amounts of CO in the stack gas is an indication that incomplete combustion is taking place in the incinerator. Incineration will be terminated if the combustion efficiency is less than 99.9%. The TNO safety officer must have access to the monitoring instruments at all times during incineration.

REGULATION 5

Operational Requirements

(1) The operation of the incineration system shall be controlled so as to ensure that the incineration of wastes or other matter does not take place at a flame temperature less than 1250 degrees centigrade, except as provided for in Regulation 4.

(2) The combustion efficiency shall be at least 99.95±0.05% based on:

$$\text{Combustion efficiency} = \frac{C_{CO_2} - C_{CO}}{C_{CO_2}}$$

where C_{CO_2} = concentration of carbon dioxide in the combustion gases

C_{CO} = concentration of carbon monoxide in the combustion gases

(3) There shall be no black smoke nor flame extension above the plane of the stack.

(4) The marine incineration facility shall reply promptly to radio calls at all times during the incineration.

REGULATION 6

Recording Devices and Records

(1) Marine incineration facilities shall utilize recording devices or methods as approved under Regulation 3. As a minimum, the following data shall be recorded during each incineration operation and retained for inspection by the Contracting Party who has issued the permit:

(a) continuous temperature measurements by approved temperature measuring devices;

(b) date and time during incineration and record of waste being incinerated;

(c) vessel position by appropriate navigational means;

(d) feed rates of waste and fuel - for liquid wastes and fuel the flow rate shall be continuously recorded; the latter requirement does not apply to vessels operating on or before 1 January 1979;

(e) CO and CO_2 concentration in combustion gases;

(f) vessel's course and speed.

(2) Approval forms issued, copies of survey reports prepared in accordance with Regulation 3 and copies of incineration permits issued for the wastes or other matter to be incinerated on the facility by a Contracting Party shall be kept at the marine incineration facility.

REGULATION 7

Control over the Nature of Wastes Incinerated

A permit application for the incineration of wastes or other matter at sea shall include information on the characteristics of wastes or other matter sufficient to comply with the requirements of Regulation 9.

2 INCINERATION OPERATIONS

2.1 Waste type and feed rates of waste to the incinerator

2.1.1 Continuous flow-measuring devices for recording liquid waste flow rate should be installed on existing marine incinerator facilities by 1 June 1980. Interim methods of control should be based on a continuous display of the waste and fuel pump status supplemented by manual checks of the type and amount of waste burned every hour, weather and sea state permitting, to be recorded in the log.

2.1.2 Where solid wastes are burned, the waste type and rate of input should be recorded in the log.

2.1.3 The feeding of wastes in containers to the incinerator will necessitate special design and operational requirements in order to comply with Regulation 5. These should include but not limited to:

.1 the waste should be fed to the incinerator at such a rate that the oxygen demand is well within the capability of the combustion air fan; and
.2 the waste should be fed to the incinerator via an air lock chamber.

2.2 Air feed to the incinerator

2.2.1 The amount of air entering the incinerator should be sufficient to ensure that a minimum of 3 per cent oxygen is present in the combustion gases near the incinerator stack exit. This requirement should be monitored by an automatic oxygen analyzer to routinely record oxygen concentrations.

2.2.2 Although existing incinerator vessels employ a fixed air input rate, marine incineration facilities may in the future use a variable air feed in which case this rate should be recorded.

2.3 Temperature controls

2.3.1 Temperature controls and records should be based on the measurement of wall temperature. Unless otherwise determined by the Contracting Party there should be three or more temperature measurement devices for each incinerator.

2.3.2 In order to comply with Regulation 5 the Contracting Party should define the operating wall temperature and the temperature below which the flow of waste to the incinerator should be automatically shut off by approved equipment.

2.3.3 The minimum wall temperature should be 1200°C unless the results of tests on the marine incineration facility demonstrate that the required combustion and destruction efficiencies specified in Regulations 3 and 5 can be achieved at a lower temperature.

2.4 Destruction efficiency

2.4.1 For the purpose of applying Regulation 3 and destruction efficiency should be determined not only for the total organic components of the wastes but additionally for particular substances such as those listed in 4.1.2.

2.5 Residence time

2.5.1 The mean residence time of the incinerator should be of the order of one second or longer at a flame temperature of 1250°C (e.g. a measured by an optical pyrometer) during normal operating conditions.

2.6 Automatic shut-off systems

2.6.1 Devices to shut off the waste feed to the incinerator in accordance with Regulation 3 should include the following:

.1 flame sensors with each burner to stop waste flow to that burner in the event of a flame-out; and

.2 automatic equipment to stop waste flow in the event of wall temperatures falling below 1200°C or the temperature determined in 2.3.3.

APPENDIX D

EVALUATION OF USE OF TEFLON® HEAT-TRACED LINE

APPENDIX D. EVALUATION OF USE OF TEFLON® HEAT-TRACED LINE

The overall objective of this task was to determine whether or not significant losses of PCBs could occur in a Teflon® transfer line between the water-cooled probe on the M/T VULCANUS and the EPA-approved sampling train.

Information in a report (10) submitted to EPA was interpreted to mean that significant losses (>90 percent) of PCBs could occur in Teflon® lines. Additional information (personal communication, M.D. Jackson with J.C. Harris of Arthur D. Little, Inc., Boston, MA, July 1982) suggested that no losses of PCBs are experienced if the sample transfer lines are held at 120°C and the length of Teflon® tube is minimized (1.8 m). Based on the above information, an evaluation was implemented to determine the degree, if any, of losses of PCBs in a 1.5-m long Teflon® line held at 120°C. Additional testing was performed at 65° to determine the effect of temperature.

A PCB-vapor generator (Figure D-1) was developed utilizing a motor driven syringe and a heated-zone volatilization chamber held at approximately 450°C. The gas was held at 200°C during dilution, but before entering the heated gas manifold which was set at 120 or 65°C. Two identical trains were set up (Train A and Train B) with the exception that Train B had a five-foot length of heat-traced Teflon® line between the glass manifold (probe) and the inlet to the EPA-PCB train. Train A was all-glass (no Teflon® line), and was connected directly to the manifold.

Eight tests were completed; four with the manifold (probe) and transfer line at 120°C and four at 65°C. In the third run at 65°C, the syringe pump was inoperative for the 1st 15 cubic feet of the sample collection. All samples were collected at 0.5 CFM.

All samples after collection were extracted with pesticide grade hexane, concentrated, and quantitated utilizing GC/ECD. The results are shown in Tables D-1 and D-2.

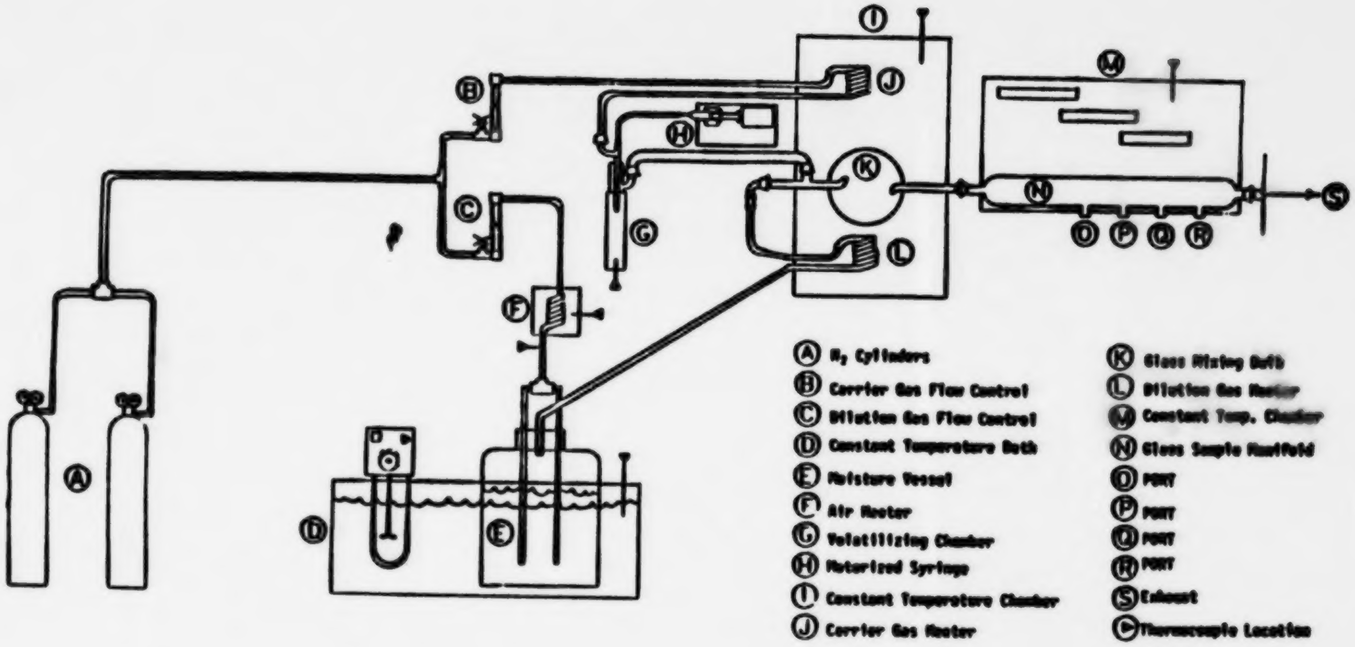

Ⓐ
Ⓑ
Ⓒ
Ⓓ
Ⓔ
Ⓕ
Ⓖ
Ⓗ
Ⓘ
Ⓙ
Ⓚ
Ⓛ
Ⓜ
Ⓝ
Ⓞ
Ⓟ
Ⓠ
Ⓡ
Ⓢ
Ⓐ N_2 Cylinders
Ⓑ Carrier Gas Flow Control
Ⓒ Dilution Gas Flow Control
Ⓓ Constant Temperature Bath
Ⓔ Moisture Vessel
Ⓕ Air Heater
Ⓖ Volatilizing Chamber
Ⓗ Motorized Syringe
Ⓘ Constant Temperature Chamber
Ⓙ Carrier Gas Heater
Ⓚ Glass Mixing Bulb
Ⓛ Dilution Gas Heater
Ⓜ Constant Temp. Chamber
Ⓝ Glass Sample Manifold
Ⓞ PORT
Ⓟ PORT
Ⓠ PORT
Ⓡ PORT
Ⓢ Exhaust
▶ Thermocouple Location

Figure D-1. PCB generation system.

TABLE D-1. DATA FROM EVALUATION OF TEFLON® HEAT-TRACED LINE

Run ID	Train B					Train A			
	Teflon Line Rinses								
	MeOH/Hexane	2nd Hexane	3rd Hexane	Back Half	Total	Total	Volume ft³ @ 0.5 CFM	Time (min)	mg/m³
120-1-A	NA[1]	NA	NA			1.422	29.485	60	1.70
120-1-B	0.359	<0.5 μg	<0.5 μg	2.520	2.879		30.018	60	3.39
120-2-A	NA	NA	NA			1.947	29.688	60	2.32
120-2-B	0.045	NN[2]	NN	2.016	2.061		30.715	60	2.37
120-3-A	NA	NA	NA			1.003	14.755	30	2.40
120-3-B	0.055	NN	NN	0.904	0.959		15.135	30	2.24
120-4-A	NA	NA	NA			4.81	14.795	30	11.48
120-4-B	0.736	NN	NN	3.076	3.812		15.260	30	8.83
65-1-A	NA	NA	NA			1.363	14.808	30	3.25
65-1-B	0.479	NN	NN	1.697	2.176		15.355	30	5.01
65-2-A	NA	NA	NA			2.209	14.814	30	5.27
65-2-B	0.509	<0.5 μg	NN	1.131	1.640		15.015	30	3.86
65-3-B	0.854	<0.5 μg	NN	2.071	2.925		30.810*	30	3.35 (6.7)
65-4-B	0.806	<0.5 μg	NN	1.608	2.414		15.337	30	5.56

*During 1st 15 cubic feet the syringe pump was not operating.

Note: 120-1-A - Manifold (probe) @ 120°C
Run one, A (all glass system)

120-1-B - Manifold (probe) @ 120°C
Teflon line @ 120°C

65-1-A - Manifold (probe) @ 65°C
Run one (all glass system)

65-1-B - Manifold (probe) @ 65°C
Run one (Teflon line @ 120°C)

[1] NA = Not Applicable.
[2] NN = Not Necessary.

TABLE D-2. % PCB FOUND IN TEFLON LINE VS. TOTAL PCB

Run ID	Teflon Line	Total	%
120-1-B	0.359	2.879	12.5
120-2-B	0.045	2.061	2.2
120-3-B	0.055	0.959	5.7
120-4-B	0.736	3.812	19.0
65-1-B	0.479	2.176	22.0
65-2-B	0.509	1.64	31.0
65-3-B	0.854	2.925	29.0
65-4-B	0.806	2.414	33.0

Based on the tests performed at 120°C, the major portion of the PCBs are collected in the back half of the PCB train and not in the Teflon® line. At lower temperatures, the PCBs condense and are collected in both the Teflon® transfer line and the back half (adsorbent and impingers) of the train.

The duplicate tests (numbers 2, 3, and 4) at 120°C indicate there is no significant difference between the PCBs collected with the all-glass (Train A) system and the second unit with the Teflon® transfer line (Train B). The difference between the amounts of PCBs collected by the two trains in the runs taken at 65°C is because of non-homogeneity in the sample concentration in the glass (probe) sample manifold. This was evident in that condensed PCB vapor was observed in the manifold near the two sampling locations.

Another significant point is that there appears to be no memory effect in the Teflon® transfer line. This was demonstrated in Test 1 at 120°C and Tests 2, 3, and 4 at 65°C.

It was concluded that there would be no irreversible loss of PCBs in the Teflon® heat-traced line planned for use during the testing onboard the M/T VULCANUS.

APPENDIX E

GLASSWARE CLEANING PROCEDURE

APPENDIX E

GLASSWARE CLEANING PROCEDURE

All glassware was cleaned [illegible] the following procedure as described in Section 3A of the 1980 issue of "Manual of Analytical Methods for Analysis of Pesticide Residues in Human and Environmental Samples".

1. Removal of surface residuals immediately after use
2. Hot soak to loosen and float most of residue
3. Hot water rinse to flush away loosened residue
4. Soak with deep penetrant or oxidizing agent to destroy traces of organic material
5. Hot water rinse to flush away materials loosened by deep penetrant soak
6. Distilled water rinse to remove metallic deposits left by the tap water
7. Acetone rinse to flush off any final traces of organic material
8. A preliminary flush of the glassware just before using with the same solvent to be used in the analysis

The following is a more detailed discussion of each cleaning step.

1. As soon as possible after use of glassware coming in contact with sample, i.e., beakers, pipets, flasks, or bottles used for standards, the glassware should be acetone-flushed before placing in the hot detergent soak. If this is not done, the soak bath may serve to contaminate all other glassware placed therein. Many instances of widespread laboratory contamination are traceable to the glassware washing sink.

2. The hot soak consists of a bath of a suitable detergent in water at 50°C or higher. The detergent, powder or liquid, should be entirely synthetic and not a fatty acid base. There are very few areas of the country where the water hardness is sufficiently low to avoid the formation of some

hard water scum resulting from the reaction between calcium and magnesium salts with a fatty acid soap. This hard water scum or curd would have an affinity particularly for the chlorinated compounds and, being almost wholly water-insoluble, would deposit on all glassware in the bath as a thin film.

There are many suitable detergents on the wholesale and retail market. Most of the common liquid dishwashing detergents sold at retail are satisfactory, but are more expensive than other comparable products sold industrially. Alconox, in powder or tablet form, is manufactured by Alconox, Inc., New York and is marketed by a number of laboratory supply firms. Sparkleen, another powdered product, is distributed by Fisher Scientific Company.

NOTE: Certain detergents, even in trace quantities, may contain organics that will contribute significant background contamination by electron capture detection. For this reason, any detergent selected should be carefully checked to ensure freedom from such contamination. The following procedure is recommended:

Add 25 mL dist. water, previously checked for background contaminants, to a 250 mL sep funnel. Add 1 drop of the liquid detergent (50 mg if in powder form), followed by 100 mL hexane. Stopper funnel and shake vigorously for 2 minutes. Allow layer separation, draw off and discard aqueous layer. Add a pinch of anhydrous Na_2SO_4 to the hexane extract and shake 1 minute. Transfer extract to a Kuderna-Danish assembly fitted with a 10 mL evaporative concentrator tube containing one 3-mm glass bead. Reduce extract volume to ca. 3 mL in a hot water bath. Cool, rinse down $\overline{\mathrm{S}}$ joint and sides of tube with hexane, diluting extract to exactly 5 mL. Stopper tube and shake on Vortex mixer 1 minute. Chromatograph by electron capture GLC and evaluate chromatogram for contaminant peaks.

3. No comments required.

4. The most common and highly effective oxidizing agent for removal of traces of organic compounds is the traditional chromic acid solution made up of H_2SO_4 and potassium or sodium dichromate. For maximum efficiency, the soak solution should be hot (40°C to 50°C). Safety precautions must be rigidly observed in the handling of this solution. Prescribed safety gear should include safety goggles, rubber gloves, and apron. The bench area where this operation is conducted should be covered with lead sheeting as spattering will disintegrate the unprotected bench surface.

The potential hazards of using chromic-sulfuric acid mixture are great and have been well publicized. There are now commercially available substitutes that possess the advantage of safety in handling. These are biodegradable concentrates with a claimed cleaning strength equal to the chromic acid solution. They are alkaline, equivalent to ca 0.1 N NaOH upon dilution and are claimed to remove dried blood, silicone greases, distillation residues, insoluble organic residues, etc. They are further claimed to remove radioactive traces and will not attack glass nor exert a corrosive effect on skin or clothing. One such product is "Chem Solv 2157," manufactured by Mallinckrodt and available through laboratory supply firms. Another comparable product is "Detex," a product of Borer-Chemie, Solothurn, Switzerland.

5, 6, and 7. No comments required.

8. There is always a possibility that between the time of washing and the next use, the glassware may pick up some contamination from either the air or direct contact. To ensure against this, it is good practice to flush the item immediately before use with some of the same solvent that will be used in the analysis.

The drying and storage of the cleaned glassware is of critical importance to prevent the beneficial effects of the scrupulous cleaning from being nullified. Pegboard drying is not recommended as contaminants may be introduced to the interior of the cleaned vessels. Neoprene-coated metal racks are suitable for such items as beakers, flasks, chromatographic tubes, and any glassware that can be inverted and suspended to dry. Small articles like stirring rods, glass stoppers and bottle caps can be wrapped in aluminum foil and oven dried a short time if oven space is available. Under no circumstance should such small items be left in the open without protective covering. The dust cloud raised by the daily sweeping of the laboratory floor can most effectively recontaminate the clean glassware.

APPENDIX F

COMPARISON OF ANALYTICAL RESULTS FROM UNIVERSITY OF NEBRASKA (UNL) AND EMSL (EPA)

APPENDIX F. COMPARISON OF ANALYTICAL RESULTS FROM UNIVERSITY OF NEBRASKA (UNL) AND EMSL (EPA)

Merrill Jackson
Environmental Protection Agency
Industrial Environmental Research Laboratory
Technical Support Staff
Research Triangle Park, NC 27711

April 4, 1983

The analytical results from UNL for TCDFs and TCDDs are reported in Appendix H and the quality assurance data and report by EMSL-RTP are presented in Appendix G. Some of the highlights to be gained from the reports include:

1. A number of sample extracts were split and analyzed by both UNL and EMSL-RTP. Comparisons of the results from these samples are given in Tables F-1 and F-3. This data demonstrates that the analytical results from the two laboratories are well within the expected range for this type of analysis. All extractions were performed by TRW and clean-up was performed at UNL. Due to the inhomogeneous nature of the samples, there was no way to accurately divide them before extraction.

2. The analysis of the quality assurance samples (Tables F-2 and F-4) were within + 50% as required by the QA plan. The overall recoveries of 2,3,7,8 TCDF in all matrices were 95% and 81% by UNL and EMSL-RTP, respectively. The TCDD recoveries were 88% and 112%, respectively, by UNL and EMSL-RTP.

3. The DEs for TCDFs were calculated only from the data generated by UNL. The analysis performed by EMSL-RTP were for QA purposes.

4. UNL found no TCDD in either the raw waste nor the emission samples at their limits of detection. EMSL-RTP at much lower limits of detection found minute amounts of TCDD in one waste and one probe rinse (and impinger), but none in the corresponding Florisil. Since the two samples did not come from the same test, no DE conclusions may be derived. The amount of TCDD found in the waste was well below levels in Agent Orange incinerated during earlier burns (0.001 vs 2.0 ppm). The amount of TCDD in the probe rinse and impinger sample amounted to 0.1 ng/m^3 whereas EPA's "Interim Evaluation of Health Risks Associated with Emissions of Tetrachlorinated Dioxins from Municipal Waste Resources Recovery Facilities" November 1982, allows up to 3.5 ng/m^3.

Several analyses are included in the UNL and EMSL reports which do not have a direct bearing on this test burn. These analyses were performed because during the analysis of the raw waste from the first PCB burn, an interference which prevented the accurate quantitation of TCDF was present. Analytical personnel felt that this problem could be eliminated by additional clean-up procedures and several samples were acquired for evaluation purposes. CWM provided a waste sample similar to the waste expected to be onboard the M/T VULCANUS during the second burn. Also, since the interference might not be in the waste for the second burn, TRW (who had waste with the interference present from the first burn available) provided portions of it for method development. Neither of these samples were taken by EPA from the ship, and no chain of custody is available. Therefore, they cannot be used to determine if the ship met DE requirements.

The requested sample sent to UNL by CWM is referred to as "Composite Vulcanus" and the TRW sample is referred to as "PCB Waste".

TRW (letter from J.F. McGaughey, copy attached) prepared the "PCB Waste" sample by mixing several of the individual samples from the first burn. The compositing was required to provide sufficient waste for method development. CWM (telephone call from George Vander Velde) does not have written records on the "Composite Vulcanus" sample. To the best knowledge of the personnel involved, the sample was taken from each tank onboard the M/T VULCANUS and composited before sending to UNL. The results of the analysis of the method development samples by UNL are attached.

Table F-1. Comparison of 2,3,7,8-TCDF Analytical Results in Incineration Sample Extracts

Test Number	TRW Number	Type of Sample	UNL Found	UNL D.L.[a]	EMSL-RTP Found	EMSL-RTP D.L.
Blank	4112	Probe Rinse	ND[b]	0.10 ng	ND	0.05 ng
3	4057/4058	Probe Rinse and Impinger Solutions	ND	1.0 ng	0.30 ng	0.05 ng
4	4063/4064		ND	0.28 ng	ND	0.10 ng
8	4093/4094		ND	0.38 ng	ND	0.05 ng
9	4099/4100		ND	0.12 ng	ND	0.04 ng
10	4105/4106		ND	0.45 ng	ND	0.05 ng
10	4109	XAD-2	ND	0.68 ng	ND	0.15 ng
3	4062	Florisil	0.57 ng	0.04 ng	0.68 ng	0.06 ng
4	4068		ND	0.06 ng	ND	0.06 ng
7	4092		ND	0.06 ng	0.15 ng	0.04 ng
8	4098		0.07 ng	0.03 ng	ND	0.04 ng
9	4104		ND	0.07 ng	ND	0.08 ng
10	4110		ND	0.03 ng	0.11 ng	0.04 ng
Blank	4116		ND	0.03 ng	ND	0.05 ng
8	4021	Raw Waste	9.0 ppb	0.30 ppb	19 ppb	0.85 ppb

a) Detection Limit

b) None Detected

Table F-2. Results of Quality Assurance Samples for TCDFs

TRW Number	Type of Sample	Spike Level	UNL		EMSL-RTP	
			Found	%	Found	%
4124/4125	Probe Rinse and Impinger Solvents	4.0 ng	3.4 ng	85	3.0 ng	75
4126/4127		2.0 ng	1.7 ng	85	1.6 ng	80
4128/4129		4.0 ng	3.5 ng	88	3.5 ng	88
4130	Florisil	2.0 ng	1.3 ng	65	1.3 ng	65
4131	"	1.0 ng	1.5 ng	150	1.0 ng	100
4132	XAD-2	1.0 ng	1.0 ng	100	1.1 ng	110
4133	"	2.0 ng	1.7 ng	85	1.5 ng	75
4134	Raw Waste	128 ppb	115 ppb	73[a]	105 ppb	73[b]
4135	"	0 ppb	25 ppb	-	11 ppb	-
4136	"	119 ppb	165 ppb	120[a]	83 ppb	60[b]
4137	"	0 ppb	20 ppb	-	11 ppb	-

a) This value is corrected for an average of 22 ppb in the waste sample.

b) This value is corrected for an average of 11 ppb in the waste sample.

Table F-3. Comparison of 2,3,7,8-TCDD Analytical Results in Incineration Sample Extracts

Test	TRW	Type of	UNL		EMSL-RTP	
Number	Number	Sample	Found	D.L.[a]	Found	D.L.
Blank	4112	Probe Rinse	ND[b]	0.12 ng	ND	0.05 ng
3	4057/4058	Probe Rinse and Impinger	ND	0.21 ng	0.18	0.05 ng
4	4063/4064		ND	0.46 ng	ND	0.05 ng
8	4093/4094		ND	0.08 ng	ND	0.05 ng
9	4099/4100		ND	0.16 ng	ND	0.06 ng
10	4105/4106		ND	0.53 ng	ND	0.05 ng
10	4109	XAD-2	ND	0.09 ng	ND	0.07 ng
3	4062	Florisil	ND	0.13 ng	ND	0.05 ng
4	4068		ND	0.19 ng	ND	0.07 ng
7	4092		ND	0.11 ng	ND	0.10 ng
8	4098		ND	0.05 ng	ND	0.11 ng
9	4104		ND	0.18 ng	ND	0.05 ng
10	4110		ND	0.17 ng	ND	0.22 ng
Blank	4116		ND	0.04 ng	ND	0.02 ng
8	4021	Raw Waste	ND	1.0 ppb	0.83 ppb	0.21 ppb

a) Detection Limit

b) None Detected

Table F-4. Results of Quality Assurance Samples for TCDDs

TRW Number	Type of Sample	Spike & Sample Level	UNL Found	UNL %	EMSL-RTP Found	EMSL-RTP %
4124/4125	Probe rinse	4.0 ng	3.4 ng	85	3.7 ng	92
4126/4127	and Impinger	2.0 ng	2.0 ng	100	2.3 ng	115
4128/4129	Solvents	4.0 ng	4.0 ng	100	3.9 ng	98
4130	Florisil	4.0 ng	2.7 ng	68	4.4 ng	110
4131	"	2.0 ng	1.5 ng	75	2.7 ng	135
4132	XAD-2	2.0 ng	1.5 ng	75	2.9 ng	145
4133	"	4.0 ng	3.4 ng	85	4.0 ng	100
4134	Raw Waste	77 ppb	75 ppb	96[a]	92 ppb	119[b]
4135	"	0 ppb	1 ppb		0.5 ppb	
4136	"	95 ppb	105 ppb	109[a]	93 ppb	97[b]
4137	"	0 ppb	1 ppb		0.4 ppb	

---

a) This value is corrected for an average of 1 ppb in the waste sample.

b) This value is corrected for an average of 0.5 ppb in the waste sample.

TRW ENVIRONMENTAL ENGINEERING DIVISION

T310.JFM.83.004
March 9, 1983

Mr. Merrill Jackson
Technical Support Staff
Industrial Environmental Research Laboratory
MD-62
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Dear Merrill:

As per our phone conversation on March 8 concerning the raw waste sample supplied to the University of Nebraska, I am including the following information.

At your request, I prepared a single bottle of waste which was shipped by "Federal Express" and received by Mike Gross on August 6, 1982. This waste sample was a composite of several individual waste samples collected onboard the VULCANUS during the PCB burn December, 1981 - January, 1982.

If you have any further questions, please call.

Sincerely,

James F. McGaughey
Laboratory Services

JFM/dh

Progress Center
3200 E. Chapel Hill Rd./Nelson Hwy.
P.O. Box 13000
Research Triangle Park, N.C. 27709 (919) 541-9100

APPENDIX

Report: "Analysis of Chemical Waste and Emissions from their Combustion for Tetrachlorodibenzodioxins and Tetrachlorodibenzofurans"

February 4, 1983

TCDD and TCDF in Chemical Waste (preliminary samples) Samples Used for Method Development

(1) Sample Identity, Date Received and their Sources of Origin.

The two samples of chemical waste for method development study were received by us on August 6, 1982. The samples arrived safely by Federal Express.

The sample labels and their sources of origin are:

a) PCB Waste (sample from Vulcanus Project): Received from J.F. McGaughey, Energy Systems Group of TRW, P.O. Box 13000, Research Triangle Park, NC 27709.

b) Composite Vulcanus Sample (from generator CWMA): Received from Chemical Waste Management, Emelle Facility, P.O. Box 55, Emille, Alabama 35459

(2) Extraction and Clean-up.

Both samples were extracted and cleaned-up during the period from August 12 to August 15 of 1982. The extraction and clean-up procedures have been described in detail in the final report entitled "Analysis of Chemical Waste and Emissions from their Combustion for Tetrachlorodibenzodioxins and Tetrachlorodibenzofurans" under the sections II. Preliminary Studies (p. 3 and 4) and III. Actual study (p. 6). The Composite Vulcanus sample was re-extracted on March 11, 1983.

(3) Analysis of Total Concentration of TCDD and TCDF by GC/HRMS and Isomer Distribution by HRGC/HRMS

a) GC/HRMS Analysis

The samples were analyzed by packed column GC/HRMS on August 20, 1983. The PCB Waste sample had TCDD and TCDF (see table 1-B of the final report). However, the recovery of the Composite Vulcanus sample was poor (ca. 25%) and, hence, the results were not reported. The re-extract of this sample was analyzed by capillary column GC/HRMS (see table 1).

b) HRGC/HRMS

The isomer distribution study was carried out using capillary GC/HRMS. During the early stages of the project Vulcanus, an SE-54 fused silica column (0.25 x 30m) was used for the isomer distribution studies. Thus, the PCB Waste sample was analyzed using the SE-54 column. However, the Composite Vulcanus sample (re-extract) was analyzed using an SP-2330 fused silica column (0.24 x 30m). Both samples had a distribution of several isomers, and an isomer with idential retention time to 2,3,7,8-TCDF was among them (see table 2).

Table 1 (Appendix). Total TCDD and TCDF Concentrations in Chemical Waste (Preliminary Samples)

Sample ID	^{13}C-level (ng)	Sample Weight(g)	Total Concentration TCDD (ppb)	Detection Limit (ppb)	Isotope Ratio 320/322	Total Concentration TCDF (ppb)	Detection Limit (ppb)	Isotope Ratio 304/306	Percent Recovery
PCB Waste[a]	5	0.5	240	40	.81	80	6	.73	70
Composite[b] Vulcanus	27	0.85	nd	6		170	7	.71	50
Composite[c] Vulcanus	5	0.5	nd	4		190	3	.71	25

a - The results reported are obtained by packed column GC/HRMS.

b - The results reported are for the re-extracted sample analyzed by capillary column GC/HRMS.

c - The results reported are for the capillary GC/HRMS analysis of the original extract. This extract gave a 25% recovery and, hence, the results were not included in Table 1-B of this final report.

Table 2 (Appendix). Relative Rentetion Times[a] of the TCDF Isomers Present in Chemical Waste (Preliminary Samples)

Sample ID	No. of Isomers	Relative Retention Time												
		1	2	3	4	5	6	7	8	9	10	11	12	13
PCB Waste[b]	8	.946	.954	.962	.971	1.000[d]	1.016	1.083	1.091					
Composite[c] Vulcanus	13	.803	.820	.859	.876	.940	.970	.988	1.000[e]	1.025	1.034	1.070	1.093	1.143

a - Retention time relative to authentic 2,3,7,8-TCDF

b - An SE-54 fused silica (0.25 x 30m) column was used for HRGC/HRMS analysis

c - An SP-2330 fused silica (0.24 x 30m) column was used for HRGC/HRMS analysis.

d - The isomer represents 30% of the total.

e - The isomer represents 20% of the total.

APPENDIX G

EMSL, EPA REPORT ON QUALITY ASSURANCE EFFORT ON ANALYSIS OF TCDFs AND TCDDs

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

DATE January 20, 1983 RESEARCH TRIANGLE PARK, N. C. 27711

SUBJECT Summary Report - Vulcanus Project

FROM Robert Harless Robert Harless
Advanced Analysis Techniques Branch, EMD/EMSL (MD-78)

TO Merrill Jackson
TSS, IERL/RTP (MD-62)

This memorandum briefly summarizes this laboratory's involvement in the Vulcanus Project, describes the HRGC-HRMS methods of analysis for TCDDs and TCDFs and presents the analytical results along with interpretations. In response to the request from the DMP, I have performed a variety of tasks associated with this project:

- Prepared and initiated the quality assurance work plan (attached).

- Coordinated the efforts of TRW, UNL and this laboratory regarding determinations for TCDFs and TCDDs.

- Subjected the $^{13}C_{12}$ - 2,3,7,8-TCDD (supplied by UNL) and tribromobiphenyl (supplied by TRW) to HRGC-HRMS analysis to determine purity and/or the presence of other compounds that would interfere with the TCDF and TCDD determinations prior to their being used in this project.

- Fortified all samples derived from this project, with exception of raw chemical waste, with specific amounts, ca. 20 ng, of $^{13}C_{12}$ - 2,3,7,8-TCDD, internal standard. This was performed in the TRW/RTP facility immediately after samples were received at RTP and prior to sample extraction procedures.

- Prepared QA samples representative of each matrice (hexane/acetone, water, Florisil, XAD-2 and raw chemical waste) as blanks and fortified samples containing specific amounts of 2,3,7,8-TCDF and 2,3,7,8-TCDD. These samples were then assigned identification numbers by TRW and interspersed with actual test samples in a "blind" fashion, i.e. there was no way for UNL or this laboratory to distinguish QA sample from test sample.

- Prepared and shipped aliquots of analytical standards (2,3,7,8-TCDD and 2,3,7,8-TCDF used to prepare QA samples and the 22 TCDD isomers) to the UNL for identification and quantification purposes.

- Performed HRGC-HRMS confirmatory analyses for TCDFs and TCDDs in "split" extracts derived from UNL clean-up procedures.

- Provided technical assistance as required.

Briefly, test samples and QA samples fortified with $^{13}C_{12}$ - 2,3,7,8-TCDD, with the exception of raw chemical waste, were subjected to TRW/RTP extraction procedures (procedures developed by UNL in accordance with QA work plan). One half of each extract was retained by TRW for PCB analysis. The other half of each extract and specific raw chemical waste samples were shipped by private aircraft to the UNL. Raw chemical waste samples were fortified with specific amounts of $^{13}C_{12}$ - 2,3,7,8-TCDD by UNL and subjected to appropriate extraction procedures. The extracts of raw waste and the extracts derived from TRW extraction procedures were then subjected to UNL clean-up procedures. Extracts were than subjected to UNL methods of analysis for TCDFs and TCDDs. Portions of specific extracts "split extracts" were shipped to this laboratory for determination of TCDFs and TCDDs using HRGC-HRMS techniques.

EPA/EMSL/RTP Method of Analysis for TCDFs and TCDDs

The Varian MAT 311A mass spectrometer used for these determinations was equipped with an eight channel hardware multiple ion selection device and was directly coupled to a capillary column, i.e. a 60m x 0.25 mm i.d. SP-2340 fused silica or a 30 m x 0.25 mm i.d. OV-101 WCOT glass column. The instrumentation, HRGC-HRMS method of analysis for 2,3,7,8-TCDD, etc. are described in the paper published in Analytical Chemistry, 52, 1239, 1980 (protocols attached). Modifications of these methods, exact masses, criteria, etc. were also used for determination of TCDFs. These modifications will be described in the following text. The HRGC-HRMS parameters were: (GC) column temperature 80°C; 8 minutes isothermal then programmed (ballistic) 34°C/min to 245°C for SP-2340 or to 265°C for OV-101: injection port 260°C; transfer lines 255°C; He flow rate 1 ml/min; (MS) ion source 250°C; specific and variable acceleration voltage, 3kV maximum; electron energy 70eV; filament emission 1 mA; mass resolution 8000 to 10000.

The exact masses used in these determinations were:

318,9793	PFK reference		292,9825	PFK reference	
333,9339	$^{13}C_{12}$ 2,3,7,8-TCDD	a	333,9339	$^{13}C_{12}$ 2,3,7,8-TCDD	b
319,8965	TCDDs	a	303,9017	TCDFs	b
321,8936	TCDDs		305,8987	TCDFs	
256,9327	TCDDs	a	240,9379	TCDFs	b
254,9856	PFK reference	a	230,9856	PFK reference	b
			373,8394	hexachlorodiphenylether	c

a and b - used for COCL loss determination.

c - used to confirm the absence of ethers which yeild fragment identical to TCDFs.

The HRGC-HRMS parameters were optimized at desired sensitivity, ca. 70% full scale deflection for 100 pg $^{13}C_{12}$ - 2,3,7,8-TCDD and 10 pg 2,3,7,8-TCDD (exact masses of m/z 334/320/322) or 100 pg $^{13}C_{12}$ - 2,3,7,8-TCDD and 10 pg 2,3,7,8-TCDF (exact masses of M/Z 334, 304, 306). The internal standard, $^{13}C_{12}$ - 2,3,7,8-TCDD and 2,3,7,8-TCDD elute simultaneously from capillary columns. The retention time (RT) was 30 minutes on the SP-2340 and 16 minutes on the OV-101. The 2,3,7,8-TCDF RT was 36 minutes on the SP-2340 and 15.5 minutes on the OV-101. A wide time window was used in these analysis for determination of TCDD and TCDF isomers, if present.

The analytical criteria used for confirmation of 2,3,7,8-TCDD and 2,3,7,8-TCDF and isomers are shown in Tables 1 and 2, respectively.

Table 1

- Correct HRGC-HRMS retention time of 2,3,7,8-TCDD
- Correct chlorine isotope ratio of molecular ions, m/z 320/322, 0.78:1
- Correct HRGC-HRMS multiple ion monitoring responses for $^{13}C_{12}$ - 2,3,7,8-TCDD and 2,3,7,8-TCDD (simultaneous responses for the respective exact masses at m/z 334 and at m/z 320/322).

- Correct responses for co-injection of sample and $^{13}C_{12}$ - 2,3,7,8-TCDD and 2,3,7,8-TCDD standard.

- Response of m/z 320/322 must be greater than 2.5 times noise level.
  Supplemental criteria applied to a number of sample extracts.

- Confirmation of COCL loss which is indicative of TCDD structure.

- Confirmation of exact masses at m/z 320/322 which correspond to elemental compositions of TCDD in real time using HRGC-HRMS peak matching technique.

TCDD isomers, if present, are also detected, recorded and confirmed. The concentration/amount are based on the concentration of 2,3,7,8-TCDD standard and the identification is based on 22 TCDD reference isomers.

Table 2

- Correct HRGC-HRMS retention time of 2,3,7,8-TCDF

- Correct chlorine isotope ratio of molecular ions, m/z 304/306, 0.78:1.

- Correct HRGC-HRMS multiple ion monitoring responses for $^{13}C_{12}$ - 2,3,7,8-TCDD and 2,3,7,8-TCDF (responses for the respective exact masses at m/z 334 and at m/z 304/306 at correct retention time and in proper chlorine isotope ratio.

- Correct responses for co-injection of sample and $^{13}C_{12}$ - 2,3,7,8-TCDD and 2,3,7,8-TCDF standard.

- Responses at m/z 304/306 must be greater than 2.5 times noise level.
  Supplemental criteria applied to a number of sample extracts.

- Confirmation of COCL loss which is indicative of TCDF structure.

- Confirmation of exact masses at m/z 304/306 which correspond to elemental composition of TCDF in real time using the HRGC-HRMS peak matching technique.

TCDF isomers, if present, are also detected, recorded and confirmed. The concentrations/amounts are based on the concentration of 2,3,7,8-TCDF standard. NOTE - It is not possible to make conclusive and valid isomer assignments because all 38 TCDF isomers are not available for reference/validation purposes. Therefore, even though the isomer detected in test sample extracts has retention time identical to 2,3,7,8-TCDF on polar and nonpolar columns the assignment of 2,3,7,8-TCDF to this isomer must be considered highly questionable.

Analytical Results

Shipments of extracts were received from UNL on 11/12/82, 11/22/82, 12/6/82 and 12/13/82. The extracts were then subjected to the previously described HRGC-HRMS multiple ion monitoring method of analysis for TCDDs and TCDFs. The COCL loss which is indicative of structure and the exact masses which correspond to respective elemental compositions of TCDD and TCDF were determined and confirmed in representative sample extracts. Also, the absence of hexachlorodiphenylethers was confirmed because these compounds yield a fragment identical to TCDF in the ionization process. The 2,3,7,8-TCDD and TCDF isomers detected in these extracts satisfied the analytical criteria described in Tables 1 and 2. Analytical results are shown in Tables 3 and 4. As indicated in the tables, approximate and small amounts of the total extracts were submitted for analysis. This prohibits reliable and accurate determination of sample preparation efficiency in the laboratory and it was not determined. The efficiency achieved for each extract should rely on UNL determinations because they had the major and/or total extract for analysis. The ratio method based on known amounts of $^{13}C_{12}$ - 2,3,7,8-TCDD, internal standard, added to each sample prior to extraction was used to determine the minimum limit of detection and the amounts of TCDD and TCDF in each extract.

In summary; the analytical data generated in this laboratory indicate:

- One TCDD isomer, 2,3,7,8-TCDD, and a unique distribution of TCDF isomers were detected in extracts of the raw waste. The 2,3,7,8-TCDD and these specific TCDF isomers were also detected in a few extracts of stack gas emissions. A comparison of the analysis of raw waste and stack gas emissions is shown in Figures 1 and 2.

- The data suggests that small amounts/concentrations of 2,3,7,8-TCDD and TCDF isomers in the raw waste were not completely destroyed in the incineration process. However, contamination of stack gas emission samples with raw waste aboard ship, sampling, transfer, sample preparation, etc. could also account for the presence of these isomers in stack gas emission samples.

- The distribution of TCDD and TCDF isomers characteristic of incineration processes was not detected in extracts of stack gas emissions. This infers that the 2,3,7,8-TCDD and TCDF isomers detected in the stack gas emission samples were not formed in the incineration process.

- One TCDF isomer in all positive test sample extracts exhibited retention time identical to 2,3,7,8-TCDF on a polar and nonpolar column. However, it is impossible to make valid and conclusive isomer assignments because all 38 TCDF isomers are not available for validation purposes.

- The analytical results generated for 2,3,7,8-TCDD and 2,3,7,8-TCDF in "blind" QA samples of the various matrices (recently decoded by you) indicate the accuracy achieved in this laboratory is within ± 50%. Also, TCDD and TCDF were not detected in blank QA samples at low minimum limits of detection. Considering the complex matrices, TRW extractions, UNL clean-ups, analysis performed on small portions of total extracts, reasonable accuracy and minimum limits of detection were achieved which can be used to validate analytical results generated for test samples in this project.

- The difference in concentrations of 2,3,7,8-TCDD and TCDF isomers in the raw waste preliminary study versus raw waste taken during incineration needs to be explained (maybe dilution factor?).

Corrective action will be taken, if necessary, after Dr. Gross, you and I evaluate the results. Then, a summary of UNL and EPA/EMSL/RTP, analytical results and interpretations will be prepared by this laboratory for DMP review. This should be done soon.

Please call me if you have any questions.

Enclosures
Tables 1 thru 4
Figure 1 and 2
QA Work Plan
  (9/7/82)
Memorandum to UNL
  (9/21, 23, 28/82)
  (11/1/82)
Memorandum to TRW
  (9/21/82)
Memorandum to you
  (12/15/82)
  (1/18/83)

cc: W. Lacy
    M. Dellarco
    J. Clements
    R. Robeson
    R. Lewis

Table 3 Analytical Results for TCDDs and TCDFs in Extracts Derived From Vulcanus Project

Sample I.D.	Matrice	Approximate Amount of Total Extract Received From UNL (%)	2,3,7,8-TCDD Detected and Minimum Limit of Detection [e] (ng)	(ng)	2,3,7,8-TCDF Detected and Minimum Limit of Detection [e] (ng)	(ng)	Total TCDF Isomers Detected, if Present, and Number of Isomers [f] (ng)	(Number)	QA (ng)	(ID)
TRW-4112 [c]	Impinger Rinse	35	ND	0.05	ND	0.05				
-4124/4125[a]	Probe/Impinger	7	3.7	0.16	3.0	0.14			4 4	2,3,7,8-TCDD 2,3,7,8-TCDF
-4105/4106[c]	"	12	ND	0.05	ND	0.05				
-4126/4127[a]	"	6	2.3	0.10	1.6	0.12			2 2	2,3,7,8-TCDD 2,3,7,8-TCDF
-4093/4094[c]	"	15	ND	0.05	ND	0.05				
-4057/4058[b]	"	10	0.18	0.05	0.30	0.05	0.57	2		
-4099/4100[d]	"	20	ND	0.06	ND	0.04				
-4063/4064[d]	"	12	ND	0.05	ND	0.10				
-4128/4129[a]	"	9	3.9	0.19	3.5	0.16			4 4	2,3,7,8-TCDD 2,3,7,8-TCDD
-4109 [a]	XAD-2	9	ND	0.07	ND	0.15				
[b]		5	ND	0.08	ND	0.11				
-4132 [a]	"	5	2.9	0.40	1.1	0.31			2 1	2,3,7,8-TCDD 2,3,7,8-TCDF
-4133 [a]	"	10	4.0	0.18	1.5	0.07			4 2	2,3,7,8-TCDD 2,3,7,8-TCDF

UNL - University of Nebraska

[a] Shipment of extracts received 11/12/82.

[b] " " " " 11/22/82.

[c] " " " " 12/6/82.

[d] " " " " 12/13/82.

[e] Analytical results are based on known amount of $^{13}C_{12}$ - 2,3,7,8-TCDD added to samples prior to extractions. Sample preparation efficiency must rely on UNL determinations because the indicated small and approximate amounts of total extracts submitted for analysis prohibit accurate determinations in this laboratory.

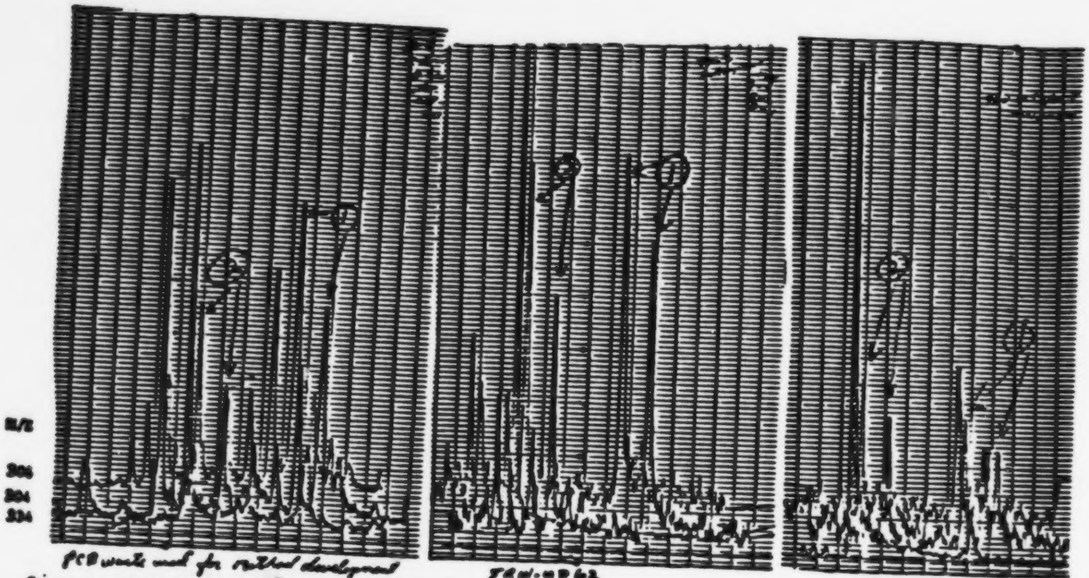
[f] Total TCDF concentration includes the isomer corresponding to 2,3,7,8-TCDF. NOTE - Conclusive and valid TCDF isomer assignment can not be made on test sample extracts because all 38 isomers are not available for reference (co-injection) purposes.

Table 4 Analytical Results for TCDDs and TCDFs in Extracts Derived From Vulcanus Project

Sample I.D.	Matrice	Approximate Amount of Total Extract Received From UNL (%)	2,3,7,8-TCDD Detected and Minimum Limit of Detection ^{f} (ng)	(ng)	2,3,7,8-TCDF Detected and Minimum Limit of Detection ^{f} (ng)	(ng)	Total TCDF Isomers Detected, if Present, and Number of Isomers ^{g} (ng)	(Number)	QA (ng)	(ID)
TRW-4110^b	Florisil	25	ND	0.22	0.11	0.04	0.17	2		
-4116^a	"	26	ND	0.02	ND	0.05				
-4130^a	"	4	4.4	1.5	1.3	0.40				
-4098^b	"	25	ND	0.11	ND	0.04			4	2,3,7,8-TCDD
-4062^a	"	12	ND	0.05	0.68	0.06	1.8	4	2	2,3,7,8-TCDF
-4131^a	"	6	2.7	0.38	1.0	0.58				
-4104^c	"	10	ND	0.05	ND	0.08			2	2,3,7,8-TCDD
-4068^d	"	26	ND	0.07	ND	0.06			1	2,3,7,8-TCDF
-4092^b	"	13	ND	0.10	0.15	0.04	0.30	3		
-4134^c	Raw Waste, 0.39 gram^h	7^e	36.0	1.5	41.0	2.0				
-4135^d	" 0.50 gram^h	3^e	0.25	0.08	5.7	0.30	8.8	5	30	2,3,7,8-TCDD
-4136^d	" 0.42 gram^h	3^e	39.0	1.9	35.0	2.3			50	2,3,7,8-TCDF
-4137^c	" 0.51 gram^h	3^e	0.20	0.05	5.6	0.50	6.7	2	40 50	2,3,7,8-TCDD 2,3,7,8-TCDF
-4021^d	" 0.47 gram^h	4	0.39	0.10	8.9	0.40	15.4	6		
-4023^d	" 0.48 gram^h	4	Not Analyzed.							
Preliminary Study	PCB Waste, 0.5 gram^h									
UNL Method Development		10	92.8	5.6	23.0	1.9	81.5	8		

UNL - University of Nebraska

a Shipment of extracts received 11-12-82.
b Shipment of extracts received 11-22-82.
c Shipment of extracts received 12-6-82.
d Shipment of extracts received 12-13-82.
e Fortified with 27 ng $^{13}C_{12}$ - 2,3,7,8-TCDD by UNL.
f Analytical results are based on known amounts of $^{13}C_{12}$ - 2,3,7,8-TCDD added to samples prior to extractions (ratio method). Sample preparation efficiency must rely on UNL determinations because the indicated small and approximate amounts of total extract submitted for analysis prohibit accurate determinations in this laboratory.
g Total TCDF concentration includes the isomer corresponding to 2,3,7,8-TCDF. NOTE - Conclusive and valid TCDF isomer assignment can not be made on test sample extracts because all 38 isomers are not available for reference.
h NOTE - These weights should be used to convert respective ng amounts to ppt or ppb concentrations, if desired.



PCB waste used for method development

TRW-4062

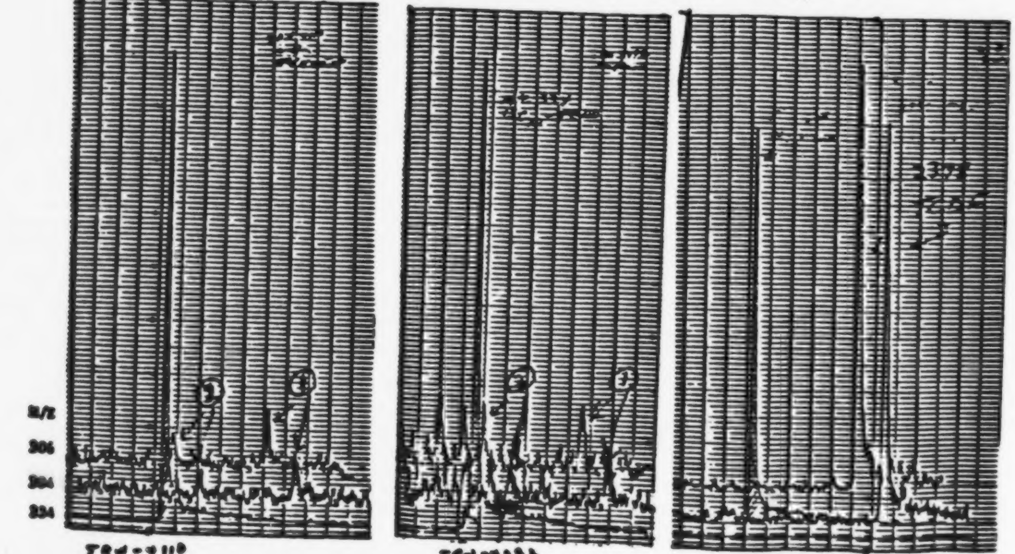
TRW-4057/4018

Figure 1. HRGC-HRMS multiple ion monitoring analyses for TCDDs

↑ indicates $^{13}C_{12}$-2378-TCDD internal standard.

①. TCDF isomer - retention time identical to 2378-TCDF.

② Prominent TCDF isomer present in most positive TW sample extracts.



TRW-4110

TRW-4092

TRW-4131 (GA)

Figure 2 HRGC-HRMS multiple ion monitoring analyses for TCDFs

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
INDUSTRIAL ENVIRONMENTAL RESEARCH LABORATORY
RESEARCH TRIANGLE PARK
NORTH CAROLINA 27711

September 7, 1982

SUBJECT: Revised Quality Assurance Plan for TCDF and TCDD
Portion of Vulcanus Incineration Test

FROM: Robert Harless Robert Harless
EMSL-EMD-AATB (MD-78)

TO: Merrill Jackson
TSS, IERL/RTP (MD-62)

The attached QA Plan for TCDFs and TCDDs which incorporates the DMP manager's comments (his memorandum also attached) is submitted to you with my approval.

Please call me if you have any questions.

cc: J. Clements
W. Lacy
M. Dellarco
R. Lewis
R. Robeson

Attachment

bm

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

August 19, 1982

OFFICE OF
RESEARCH AND DEVELOPMENT

SUBJECT: QA Plan for Vulcanus Incineration Test

FROM: Michael J. Dellarco, Project Manager MD
Quality Assurance Management Staff (RD-680)

TO: Robert Harless, Chemist
Advanced Analtyical Techniques Branch, EMSL-RTP

THRU: William J. Lacy, Director
Water and Waste Management Monitoring
Research Division (RD-680)

Pursuant to Dioxin Monitoring Program (DMP) support for the incineration of chemical wastes at sea aboard the Vulcanus, I have reviewed your draft quality assurance plan for the analyses of emission samples. The plan is clear and concise, yet contains all of the details concerning how samples will be analyzed. The quality assurance procedures listed in the plan to ensure that the analyses are valid have been demonstrated in the past to be highly reliable.

For purposes of clarification, I would suggest you consider including the following additional points in the revised QA Plan:

- Note that samples will be analyzed only if they are shipped by a carrier approved to handle hazardous materials by the Department of Transportation.
- Note that only those samples received in good condition with appropriate chain of custody documents will be analyzed.
- Outline corrective action procedures which will be implemented if some sample analyses are indeterminate; perhaps noting that initial results will be discussed with Dr. Gross, and that re-extraction and re-analysis of the sample(s) in question will be conducted, is the most satisfactory statement for the QA Plan.
- Note that the two laboratories will evaluate the results of analyses jointly once the data are decoded by the project manager.

I sincerely appreciate the capable management you have demonstrated in initiating this project for the DMP and look forward to its successful completion. Please continue to keep Ross Robeson and me updated with periodic status report.

Analysis of Samples from Second Trial PCB Burn Aboard the M/T Vulcanus for TCDFs and TCDDs

Quality Assurance Plan

A quality assurance (QA) plan has been prepared for this project in regards to monitoring efforts for tetrachlorodibenzofurans (TCDFs) and tetrachlorodibenzo-p-dioxins (TCDDs). The primary objective of this specific study is to determine the destruction efficiency for TCDFs and secondarily for TCDDs. In order to determine a valid destruction efficiency value, the concentrations of TCDFs and TCDDs in the chemical waste (PCB contaminated fuel oil) being incinerated and the emissions from the incinerator stack must be known. TCDFs and TCDDs can also be formed in incineration processes. Fortunately, the distribution of isomers in raw material and emissions are usually quite different and the source should be readily apparent. Quantitative determinations for pg/g and ng/g levels of TCDFs and TCDDs require sensitive, specific, and validated analytical procedures in order to generate meaningful and valid data for assessment purposes. The analytical methodology that will be used for these determinations is sensitive and specific. However, it has not been validated for the complex sample matrices that will be encountered in this unique experimental project. In fact, it would be extremely difficult, if not impossible, to duplicate the test burn conditions in the laboratory. Therefore, stringent measures are incorporated to assure the analytical data derived from these procedures are valid and scientifically sound. This will be accomplished in the following manner:

- Only those samples received in good condition with appropriate chain of custody documents will be analyzed in this study. Approved shipping containers and air carriers should be used to transport samples to respective destinations.

- Analytical methodology used for quantitative determination of TCDFs and TCDDs in the chemical waste, Florisil and XAD-2 will be validated prior to analysis of actual samples.

- ^{13}C-2,3,7,8-TCDD, internal standard, will be added to each sample in order to determine and validate the analytical methodology efficiency for each sample that is analyzed. Documented experience has shown that it can be used for this purpose (for TCDFs) with confidence. Unfortunately, labeled TCDFs are not commercially available.

- QA samples consisting of blanks and respective sample matrices fortified with 2,3,7,8-TCDF and TCDD will be submitted "blind" along with test samples to the analytical laboratory in order to verify and validate the procedures and results.

- Stringent analytical criteria will be used for confirmation of TCDF and TCDD residues.

- Valid minimum limits of detection will be determined for assessment purposes.

- The analytical determinations will be performed by two laboratories (University of Nebraska and EPA-EMSL-RTP).

- Analytical results from both laboratories will be submitted to the Project Manager upon completion of project. QA and test samples will then be decoded and identified and the two laboratories will jointly evaluate the results.

- Based upon the two laboratories' evaluation of analytical data, corrective action procedures, i.e., re-extraction and/or re-analysis of specific samples/extracts will be initiated if necessary.

This is a collaborative effort between the University of Nebraska (UN) and EMSL-RTP. UN will develop and validate the required analytical methodology, perform all extractions, cleanups, and analysis. EMSL-RTP will institute QA measures and perform confirmatory HRGC-HRMS analysis on split portions of UN extracts.

Contact Personnel

EMSL-RTP: R. L. Harless (919) 541-2248 (FTS 629-2248)
UN: M. L. Gross 402-472-2794 (FTS 622-7211, Ext. 2794)

Development and validation of analytical methodology (extraction, cleanup, and analysis) for quantitative determination of pg/g and ng/g levels of TCDFs and TCDDs in representative samples of the chemical waste, Florisil and XAD-2 are now in progress at the University of Nebraska. Representative samples of each matrice will be fortified with ^{13}C-TCDD prior to extraction in order to determine and validate the analytical methodology efficiency. Specific samples will also be fortified with 2,3,7,8-TCDF and TCDD in order to validate the procedures. The validated extraction procedures will be used by TRW on the stack samples. The description and number of analyses involved in this phase of the work is shown:

- Chemical waste (fuel oil) - 6 analyses

- Florisil - 2 analyses

- XAD-2 - 2 analyses

The Vulcanus incineration test will begin around August 16, 1982, and will be completed about the first week of September. Samples collected during this test will then be shipped to TRW located at Research Triangle Park, NC. EMSL-RTP will fortify each test sample and QA samples with 10 to 50 ng of ^{13}C-2,3,7,8-TCDD, internal standard. QA samples will also be fortified with ppt to ppb levels of 2,3,7,8-TCDF and TCDD. TRW will extract the samples. Each extract will be split, 50% will be shipped to UN for cleanup and analysis and TRW will retain 50% for their PCB determinations. Representative samples of the chemical waste (fuel oil) that was incinerated will also be shipped to UN for extraction, cleanup, and analysis. Samples involved in this project are described:

- 6 chemical waste (fuel oil) samples
- 12 air sampler impingers/rinses
- 6 Florisil
- 3 XAD-2
- 9 QA (3 impingers, 2 Florisil, 2 XAD-2, 1 chemical waste, 1 standard solution of 2,3,7,8-TCDF and TCDD).
- 8 UN internal QA (two chemical waste samples, one Florisil method check, 5 method checks (blanks).

Basic analytical procedures utilized by UN are described in the attached reference(1). The basic procedures were modified, refined, and validated for quantitative determination of TCDFs and TCDDs in complex and specific sample matrices encountered in this experimental project; i.e., high resolution WCOT capillary columns are used to provide specificity in HRGC-HRMS determinations performed at 7500 mass resolution, multiple ion monitoring HRGC-HRMS determinations are performed using the exact masses corresponding to M/Z 304 and 306 of TCDFs, M/Z 320 and 322 of TCDDs and the M/Z 332 of ^{13}C-TCDD-internal standard. The instrumentation is calibrated daily using TCDF, TCDD and labeled TCDD standards, Internal QA, for this project consists of one method check for every four samples, one Florisil method check; two chemical waste samples fortified with TCDF and TCDD concentrations twice as high the actual concentrations found in the samples.

The HRCG-HRMS detection technique for TCDDs which is used by EMSL-RTP is described in the attached reference(2). With the following modifications, the exact masses of M/Z 304 and 306 corresponding to TCDFs and M/Z 332 corresponding to ^{13}C-2,3,7,8-TCDD internal standard are monitored in order to perform the determinations for TCDFs. The instrumentation calibration/sensitivity is determined daily using 2,3,7,8-TCDF, 2,3,7,8-TCDD and ^{13}C-2,3,7,8-TCDD standards.

The analytical criteria that will be used for confirmation of TCDDs is described in the two attached references (1,2). The analytical criteria that will be used for confirmation of TCDFs are:

- HRGC-HRMS retention time frame.

- Correct molecular ion chlorine isotope ratio
- Confirmation of exact masses corresponding to elemental composition of TCDF.
- Response of M/Z 304 and 306 must be greater than 2.5X noise level.
- HRGC-HRMS analysis to confirm the absence of exact masses of M/Z 374 and 376 corresponding to hexachlorodiphenylethers at sensitivity equal to TCDF analysis.
- COCl loss analysis will be performed on a representative number of samples.

Quantification of TCDDs is based on te concentration of 2,3,7,8-TCDD analytical standard and is described in the two attached references (1,2). All 22 TCDD isomers are available for identification purposes. Quantification of TCDFs is based on the concentration of 2,3,7,8-TCDF analytical standard. Conclusive isomer assignments cannot be made because only 1 of the 38 possible TCDF isomers is available for reference purposes. The analytical results obtained for TCDDs and TCDFs are corrected for analytical methodology efficiency (recovery of ^{13}C-2,3,7,8-TCDD internal standard).

Minimum limits of detection for TCDFs and TCDDs will be determined based on MS sensitivity, analytical methodology efficiency, sample size/volume, aliquot of total extract used in analysis and 2.5 times noise level.

The limits of detection from this procedure should be sufficient to permit the calculation of a DRE of 99.9% based on a level of 1 ppm of either TCDF or TCDD in the chemical waste.

Analytical methodology efficiency should be greater than 33%. Precision and accuracy should be greater than ± 50%.

In summary, it is emphasized that this is an experimental project which would be quite difficult to duplicate in the Laboratory. Therefore, it is quite impossible to use analytical methodology that has been previously validated for the specific sample matrices and environmental conditions encountered. The use of state-of-the-art analytical procedures, stringent QA measures, analytical criteria, and multiple laboratory participation will provide scientifically sound and valid data for assessment purposes.

Other CDFs, CDDs, and air sampling device collection and retention efficiency are not addressed in this work plan. However, the sampling device collection and retention efficiency for 1,2,3,4-TCDD has been determined under stack conditions.

References

1. Gross, M.L., T. Sun, P.A. Lyon, S.F. Wojinski, D. L. Hilkers, A.K. Dupray, Jr., and R.G. Heath, "Method Validation for the Determination of Tetrachloridibenzodioxin at the Low Parts-per-Trillion Level". Anal. Chem. 53 1902-1906 (1981)

2. Harless, R.L., E.O. Oswald, M.K. Wilkinson, A.E. Dupuy, Jr., D. D. McDaniel and H. Tai, "Sample Preparation and Gas Chromatography - Mass Spectrometry Determination of 2,3,7,8-Tetrachlorodibenzo-p-dioxin". Analy. Chem 52 1239-1245 (1980).

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
RESEARCH TRIANGLE PARK
NORTH CAROLINA 27711

September 21, 1982

Dr. Michael Gross
Department of Chemistry
University of Nebraska
Lincoln, Nebraska 68588

Dear Dr. Gross:

I used the 1 ng/µl standard solution of $^{13}C_{12}$-2,3,7,8-TCDD (^{13}C-TCDD), internal standard, supplied by your laboratory to fortify each of the Vulcanus Test Burn samples and the Quality Assurance (QA) samples. The samples were then subjected to the TRW extraction procedures. You are receiving 50% of each extract which needs to be concentrated and subjected to your specific cleanup procedures prior to HRGC-HRMS analysis for TCDFs and TCDDs. The TRW identification numbers, sample matrice, solvents and ^{13}C-TCDD fortification levels are indicated in the accompanying TRW shipment letter.

Aliquots of the analytical standards that were used for fortification and QA purposes in this project are packed in a separate container and identified. These are for your calibration/quantification purposes. Also, aliquots of the 2:2 and 3:1 type TCDDs and necessary chromatograms are enclosed for identification purposes.

- 1.2 ml of 20 pg/µl 2,3,7,8-TCDD standard.
- 1.2 ml of 50 pg/µl 2,3,7,8-TCDF standard.
- 130 µl of 2:2 type TCDDs, 10 pg/µl approximate concentration.
- 130 µl of 1,2,3,4- and 3:1 type TCDDs, 10 pg/µl approximate concentration.
- 130 µl of 100 pg/µl $^{13}C_{12}$-2,3,7,8-TCDD, internal standard.

Samples of raw chemical waste are also enclosed.

- TRW 4134 0.38865 gms in 1.0 ml toluene and 1.5 ml benzene.
- TRW 4135 0.50110 gms in 1.0 ml toluene and 1.5 ml benzene.
- TRW 4136 0.42272 gms in 1.0 ml toluene and 2.0 ml benzene.
- TRW 4137 0.50994 gms - No solvents.

The cleanup and analysis sequence should be, XAD-2, Florisil, impinger, probe rinse and raw chemcial waste in order to avoid potential problems. I will provide you with the specific TRW ID numbers (extracts) that are to be analyzed in sequence in this project. Aliquots "splits" of all positive extracts should be submitted to me for confirmation analysis.

Please review the analytical criteria to be used for confirmation of TCDFs and TCDDs in the attached protocol. Please call if you have any questions.

Sincerely yours,

Robert Harless, Research Chemist
Advanced Analysis Techniques Branch
Environmental Monitoring Division

Attachment

cc: W. Lacy
M. Dellarco
M. Jackson
J. Clements
R. Lewis
R. Robeson

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

DATE January 18, 1983 RESEARCH TRIANGLE PARK, N. C. 27711

SUBJECT Preliminary Data - Vulcanus Project

FROM Robert Harless
Advanced Analysis Techniques Branch, EMD/EMSL/RTP (MD-78)

TO Merrill Jackson
TSS, IERL/RTP (MD-62)

The preliminary data generated in this laboratory that you requested is attached (it was given to you 1-11-83). As you know, this data and data generated by UNL should be evaluated by Dr. Gross, you and I so that corrective action can be taken if necessary. This laboratory's summary report is being prepared now.

Please call me if you have any questions.

Attachments
Table 1
Table 2

cc: W. Lacy
M. Dellarco
R. Robeson
J. Clements
R. Lewis

Table 1. Analytical Results for TCDDs and TCDFs in Extracts Derived From Vulcanus Project

Sample ID	Approximate Amount of Total Extract Received From UN (%)	2,3,7,8-TCDD Minimum Detection Limit (ng)[c]	2,3,7,8-TCDD Detected (ng)[c]	2,3,7,8-TCDF Minimum Detection Limit (ng)[c]	2,3,7,8- TCDF Detected (ng)[c]	Total TCDF Isomers Detected if Present and Number of Isomers (ng)	(Number)
TRW-4062[a]	12	0.05	ND	0.05	0.68	1.8	(4)
-4109[a]	9	0.07	ND	0.15	ND		
-4116[a]	26	0.02	ND	0.05	ND		
-4130[a]	4	1.3	4.4	0.40	1.3		
-4131[a]	6	0.38	2.7	0.58	1.0		
-4132[a]	5	0.40	2.9	0.31	1.1		
-4133[a]	10	0.18	4.0	0.07	1.5		
-4124/4125[a]	7	0.16	3.7	0.14	3.0		
-4128/4129[a]	9	0.19	3.9	0.16	3.5		
-4126/4127[a]	6	0.10	2.3	0.12	1.6		
PCB Waste Preliminary Study[a]	10	5.6	92.8	1.9	23.0	81.5	(8)
TRW-4109[b]	5	0.08	ND	0.11	ND		
-4092[b]	13	0.10	ND	0.04	0.15	0.54	(4)
-4098[b]	25	0.11	ND	0.04	ND		
-4110[b]	25	0.22	ND	0.04	0.11	0.17	
-4126/4127[b]	15	Duplicate Sample - Not Analyzed					
-4057/4058[b]	10	0.05	0.18	0.05	0.30	0.57	(2)

UN - University of Nebraska

[a] Shipment of extracts received 11-12-82.
Each total extract theoretically contained 10ng ^{13}C-2,3,7,8-TCDD, internal standard.

[b] Shipment of extracts received 11-22-82.
Each total extract theoretically contained 10ng ^{13}C-2,3,7,8-TCDD, internal standard.

[c] Analytical results corrected for sample preparation efficiency.

[d] Total TCDF including the isomer corresponding to 2,3,7,8-TCDF. NOTE - Valid and conclusive TCDF isomer assignment can not be made on the test sample extracts because all 38 isomers are not available for validation purposes.

Table 2. Analytical Results for TCDDs and TCDFs in Extracts Derived From Vulcanus Project.

Sample ID	Approximate Amount of Total Extract Received From UN (%)	2,3,7,8-TCDD Minimum Detection Limit (ng)[c]	2,3,7,8-TCDD Detected (ng)[c]	2,3,7,8-TCDF Minimum Detection Limit (ng)[c]	2,3,7,8- TCDF Detected (ng)[c]	Total TCDF Isomers Detected if Present and Number of Isomers (ng)	(Number)
TRW-4134[a]	7	1.5	36	2.0	41		
-4135[a]	8	Insufficient extract for analysis.					
-4136[a]	7	-	-	-	-		
-4137[a]	3	0.05	0.20	0.50	5.6	6.7	(2)
The above samples were fortified with 27ng ^{13}C-2,3,7,8-TCDD internal standard.							
-4112[a]	35	0.05	ND	0.05	ND		
-4105/4106[a]	12	0.05	ND	0.05	ND		
-4093/4094[a]	15	0.05	ND	0.05	ND		
-4104[a]	10	0.05	ND	0.08	ND		
-4135[b]	3	0.08	0.25	0.30	5.7	8.8	(5)
-4136[b]	3	1.9	39.0	2.30	35.0		
-4068[b]	26	0.07	ND	0.06	ND		
-4063/4064[b]	12	0.05	ND	0.10	ND		
-4099/4100[b]	20	0.06	ND	0.04	ND		
-4021[b]	40	0.10	0.39	0.40	8.9	15.4	(6)
-4023[b]	4	-	-	-	-		

UN - University of Nebraska

[a] Shipment of extracts received 12-6-82.

[b] Shipment of extracts received 12-13-82.
With the noted exceptions, the total extract theoretically contained 10ng ^{13}C-2,3,7,8-TCDD, internal standard.

[c] Analytical results corrected for sample preparation efficiency.

[d] Total TCDF concentration including isomer corresponding to 2,3,7,8-TCDF. NOTE - Valid and conclusive TCDF isomer assignment can not be made on the test sample extracts because all 38 isomers are not available for validation purposes.

APPENDIX H

UNIVERSITY OF NEBRASKA-LINCOLN REPORT ON ANALYSES OF TEST SAMPLES FOR TCDFs AND TCDDs

Report

"Analysis of Chemical Waste

and

Emissions from their Combustion

for

Tetrachlorodibenzodioxin and Tetrachlorodibenzofurans"

by

Midwest Center for Mass Spectrometry
Department of Chemistry
University of Nebraska
Lincoln, Nebraska 68588

February 4, 1983

Michael L. Gross
Professor and Director

N.C.A Weerasinghe

N.C.A. Weerasinghe
Postdoctoral Associate

I. Introduction

This study is directed at determining the levels of tetrachlorodibenzodioxin (TCDD) and tetrachlorodibenzofurans (TCDF) in chemical waste oil and in corresponding emission samples collected during the combustion of the chemical waste. The analyses were conducted in two stages. The first stage employed packed column gas chromatography/high resolution mass spectrometry. This analysis provides optimum certainty that the materials detected have the chemical formulae $C_{12}H_4O_2Cl_4$ and $C_{12}H_4OCl_4$ but little certainty in terms of isomer composition. The second stage of the analysis made use of capillary column gas chromatography/high resolution mass spectrometry. This analysis permits determination of the fraction of total TCDD which is the highly toxic 2, 3, 7, 8-isomer and an assignment of the isomer distribution. Similar data were gathered for the tetrachlorodibenzofurans; however, the data are not unambiguous because the TCDF isomers (except for 2, 3, 7, 8-TCDF) were not available.

Prior to beginning the actual analysis, method development research was carried out. Specifically, a procedure for cleaning up chemical waste containing high levels of PCBs was developed to permit detecting 100-500 picogram quantities of TCDD and TCDF in 0.5 to 1.0 g of a chemical waste sample. Secondly, measurements were made to verify a solvent-of-choice for efficiently extracting TCDD and TCDF from the Florisil and XAD resins which were used in emission sample collection.

The first section of this report is a description of the method development research. The second part contains a description of the procedures used to extract and/or cleanup the real samples and controls and the actual analytical data.

II. PRELIMINARY STUDIES

A. Verification of Solvent for Soxhlet Extraction Procedure

The XAD resin and Florisil samples were extracted using a Soxhlet apparatus. Prior to adding the sample, silica gel was placed in the sample cup and hexane was added to the Soxhlet. The solvent was allowed to cycle for about four to five hours before it was discarded.

The resin and Florisil samples (approx. 5 g), spiked with the internal standard (C^{13}- 2, 3, 7, 8-TCDD), 2, 3, 7, 8-TCDD and 2, 3, 7, 8-TCDF were placed in the sample cup on top of a layer of the pre-extracted silica gel. Hexane (150 ml) was cycled through the sample for 24 hours for extraction. The hexane extract was then concentrated to a volume of 60 ml in order to proceed with further clean-up.

Conclusions

For XAD resin, all three solvents appeared to be equally efficient. However, hexane was recommended as the solvent for extraction since its easier to handle in the work-up of samples.

For Florisil, 10% benzene in hexane appeared to be somewhat better than hexane. However, since the difference in the recoveries of the two solvents was not significant, hexane was recommended as the solvent for Soxhlet extraction of Florisil (Table 1-A).

B. Method of Extraction and Clean-up for Chemical Waste

The chemical waste sample was weighed (ca. 0.5g)and spiked with the internal standard C^{13}-2,3,7,8-TCDD (5ng). The sample was dissolved in 15 ml of acetonitrile and quantitatively transferred to a separatory funnel. 50ml of distilled water was added to the separatory funnel and the aqueous solution was extracted with three 30ml portions of hexane. The hexane was used to rinse the sample jar before adding to the separatory funnel for extraction. The hexane extracts were combined.

The combined hexane extract was washed with six 15ml portions of concentrated sulfuric acid followed by 30ml of water. A small amount of Na_2CO_3 was added to neutralize any trace of acid left and the hexane was finally washed with another 30ml of water. Subsequently, the hexane extract was transferred to a 50 ml jar and dried with anhydrous Na_2SO_4. The extract was finally concentrated to a volume of 5 ml in a sample jar and submitted to "Alumina Chromatography-I".

(1) Alumina Chromatography-I

A 15 x 1 cm^2 alumina column packed in glass was used in the chromatography. Alumina was washed with CH_2Cl_2 and activated at 160°C overnight prior to use.

Alumina was packed in hexane and capped with a 2 x 1 cm^2 layer of anhydrous Na_2SO_4. The hexane extract (5ml) was transferred to the top of the column. The transfer was aided by two additional 25ml portions of hexane which were used to rinse the jar. The column was subsequently washed with 30ml of CCl_4 followed by 30ml of 10% CH_2Cl_2 in hexane. The pre-washings were discarded. The TCDD and TCDF were eluted from the alumina with 50ml of 25% CH_2Cl_2 in hexane. Finally, the higher CDD's and CDF's were eluted off the column with 50ml of CH_2Cl_2 and this fraction was concentrated to a volume 2-3 ml and stored for analysis at a later date if necessary. The 25% CH_2Cl_2 fraction was virtually evaporated to dryness under dry nitrogen. The residue was dissolved in 1-2 ml of hexane and submitted to "Alumina Chromatography-II".

(2) Alumina Chromatography-II

The alumina was washed and activated in the manner already described. A disposable pipette was plugged with glass wool and packed with alumina up to a height of 4 cm. The alumina was capped with 1/4 cm layer of anhydrous Na_2SO_4.

The column was initially wetted with hexane, and the eluate from "Alumina Chromatography -I" was transferred to the top of the column. The transfer was aided with an additional 5 ml of hexane. The alumina was washed with 4ml of 10% CH_2Cl_2 in hexane, and finally the TCDD and TCDF were eluted with 5 ml of 25% CH_2Cl_2 in hexane. The final eluate was collected in two fractions. Fraction 1, which was equivalent to 1.5 ml of 25% CH_2Cl_2, was later discarded. The Fraction 2, which was consisted of 3.5 ml of 25% CH_2Cl_2, was collected and concentrated under dry nitrogen while the solvent was being replaced with hexane (100μl).

(3) Conclusions

The percent recoveries of the C^{13}-2,3,7,8-TCDD internal standard was in the range of 70 to 80%. Both TCDD and TCDF were detected in the ppb range at detection limits ranging from 10-50 ppb. The higher detection limits were due to chemical noise. It was evident that, in order to improve the detection limits, further clean-up was necessary (Table 1-B).

The samples were spiked with 5 ng of the C^{13}-internal standard. However, it was evident that the level of spike needed to be increased to 20-30ng in order to improve on the accuracy of the detection of TCDD and TCDF.

III. ACTUAL STUDY - EXTRACTION AND CLEAN-UP

A. Clean-up Procedures for Florisil, XAD Resin, Impinger and Probe Rinses

The hexane extracts (from the Soxhlet procedure) of the samples were prepared elsewhere and shipped to us. The sample volumes were in the range of 250 to 1000 ml. The extracts were evaporated to a volume of 70 to 100 ml under dry nitrogen before clean-up. The hexane extract was transferred to a separatory funnel and washed twice with 25 ml of 1F KOH, then once with 25 ml of distilled water. The hexane layer was subsequently washed with 10-15 ml portions of concentrated sulfuric acid until both the hexane and acid layers were clear. The extract (organic layer) was finally washed with two 25 ml portions of distilled water and concentrated to a final volume of 1-2 ml under dry nitrogen.

(1) Alumina Chromatography

Alumina was washed and activated in the manner already described (p. 3). A 5 cm column was prepared using a disposable pipette plugged with glass wool. The alumina was capped with 1/4 cm layer of anhydrous Na_2SO_4.

Hexane was used to wet the column before transferring the sample. The jar was rinsed with one ml of hexane which was transferred to the column. The alumina was eluted with 6 ml of pesticide grade CCl_4, then with 4 ml of 10% CH_2Cl_2 in hexane and finally with 6 ml of 25% CH_2Cl_2 in hexane. The methylene chloride/hexane fraction was collected and concentrated under dry nitrogen while replacing the volatile CH_2Cl_2 with hexane. All other fractions were discarded.

B. Chemical Waste- Extraction and Clean-up

The extraction and clean-up procedure was similar to that described under preliminary studies. However, it was evident from the preliminary analyses that further clean-up was necessary to lower the detection limits. In order to improve the clean-up, a silica chromatography step was introduced after the two stages of alumina chromatogrphy already described.

(1) Silica Chromatography

Silica chromatography was carried out in a disposable pipette. The silica was not activated before use.

A 5 cm column was prepared in a pipette plugged with glass wool. The silica was capped with 1/4 cm layer of anhydrous Na_2SO_4. The column was wetted with hexane before transferring the sample. The sample from "Alumina Chromatography-II" (fraction 2) in hexane was transferred to the column. An additional 5 ml of hexane was used to rinse the sample jar before being transfered to the column. The TCDD and TCDF were eluted with 3.5 ml of 20% benzene in hexane. The hexane pre-wash was also combined to the final fraction and concentrated to a final volume of 100 µl under dry nitrogen for analysis.

List of Materials Used in Sample Extraction

Acetone, OmniSolv, MCB

Benzene, OmniSolv, MCB

Carbon tetrachloride, Omnisolv, MCB

Ethyl alcohol, OmniSolv, MCB

Hexane, OmniSolv, MCB, non UV

Methylene chloride, OmniSolv, MCB

Sulfuric acid, concentrated, analytical reagent, Mallinckrodt

Water, distilled in glass

Potassium hydroxide, analytical grade, Mallinckrodt

Sodium sulfate (anhydrous), analytical grade, Fisher

Sodium carbonate, (anhydrous), analytical grade, Fisher

Aluminum oxide, neutral, activity grade I, Woelm Pharma

Silica gel, 60-200 mesh, reagent grade, Baker Chemical Co.

Dry nitrogen (boil-off from liquid N_2)

IV. TOTAL TCDD ANALYSES BY PACKED COLUMN GC/HRMS

The sample extracts to be analyzed were kept in centrifuge tubes in a freezer at -4°C. At the time of analysis, the inside of the tubes was washed with hexane or isooctane (approximately 100 μl was used). Subsequently, the solvent was allowed to evaporate to approximately half of its original volume. The remainder was accurately measured with a graduated Hamilton syringe, a major portion (approximately 3/4) returned to the centrifuge tube, and the amount remaining in the syringe was used for GC/HRMS analysis.

A. Mass Spectrometer

A Kratos MS-50 ultra-high resolution mass spectrometer was used for this analysis (ultimate resolution, 210,000). The mass spectrometer was interfaced via a jet separator to a Perkin Elmer Sigma-II gas liquid chromatograph. A multiple peak monitoring (MPM) accessory was used which enabled us to monitor three ions on three channels. The data acquisition was accomplished with a Nicolet Model 1170 signal averaging computer.

B. Gas Chromatography

A glass column (6' x 1/4" O.D.) containing HNU Permabond methyl silicone coated with o.6% poly S-179 (HNU Systems, Inc.) was used in the analysis. Typical operating conditions of the gas chromatograph were: Helium flow rate of 25 ml/min., injector 275°C, column temperature program: initial at 250°C and programmed at 10°C/min. to 275°C and held at the final temperature until TCDD had eluted.

The GC/HRMS interface was a simple glass lined stainless steel capillary which was coupled to a glass jet separator. The interface was held at a temperature of 250°C. Typical retention time were 3.2 and 3.3 minutes for 2, 3, 7, 8-TCDD and 2, 3, 7, 8-TCDF respectively (peak width at 10% height approximately 50 seconds).

C. Mass Spectrometric Conditions

The electron impact source was used at 70eV ionizing energy and an accelerating voltage of 8KV. The source was set up at 260°C. The instrument was tuned to a resolving power of 10,000 (10% valley definition).

Three ions were monitored using the peak matching accessory, at m/z 319.8965, m/z 321.8936, and m/z 333.9339. The ions at m/z 322 and m/z 320 are the most abundant and the second most abundant, respectively, molecular ions of TCDD and m/z 334 is ^{13}C-2, 3, 7, 8-TCDD, the internal standard. For TCDF analysis, a second injection was made, and the ions monitored were m/z 303.9016, 305.8986 and 333.9339. Complete peak profiles were acquired at an amplifier bandwidth of 300Hz by scanning at a frequency of about 2Hz, corresponding in each case to a mass range of 300 ppm (0.096 amu). The output of the mass spectrometer was accumulated over about 75 sweeps per channel using a Nicolet Model 1170 signal averager. The resulting signals were submitted to a three-point smoothing routine prior to print out on an X-Y recorder. All the data were acquired as hard copies and also stored on magnetic tape.

D. Calculation of Results

Quantification was achieved using the internal standard ratio method. Throughout the experiment, standard samples containing 2, 3, 7, 8-TCDD, 2, 3, 7, 8-TCDF and ^{13}C-2, 3, 7, 8-TCDD were analyzed. The slopes of the calibration plots were taken as the averages of the ratios of $(I^{334}/ng)/(I^{322}/ng)$ for TCDD and $(I^{334}/ng)/I^{306}/ng)$ for TCDF obtained using the standard samples.

Residue levels of TCDD and TCDF in actual samples were calculated by comparing the ratios of intensities of I^{322}/I^{334} (for TCDD) and I^{306}/I^{334} (for TCDF) obtained for a given sample with the slope of the calibration plot. The detection limit was considered to be the respective value obtained for an intensity of 2.5 x noise level measured at the base line.

The internal standard (^{13}C-2, 3, 7, 8-TCDD) was utilized in the calculation of percent recoveries, and in doing so the absolute intensity (I^{334} normalized) was measured and compared with the intensities (I^{334}/ng) obtained by injecting standard solutions of the internal standard.

E. Validation

Results which indicated the presence of TCDD and TCDF were validated by comparing the signal intensities of m/z 319.8965, m/z 321.8936 for TCDD, and 303.9016, 305.8986 for TCDF; most abundant ions of TCDD and TCDF. The theoretical ratio of m/z 320/322 or 304/306 is 0.77. Validation of TCDD and TCDF is considered acceptable if the observed ratio of signals is 0.77 ± .10. The results are summarized in Table 6.

V. TCDD AND TCDF ANALYSIS BY CAPILLARY COLUMN GC/HRMS

Appropriate dilutions of the samples were made with hexane at the time of analysis and the aliquots from the resulting solutions were used for capillary column GC/HRMS.

A. Gas Chromatography/Mass Spectrometer

A Kratos MS-80 medium resolution mass spectrometer (ultimate resolution 20,000), equipped with a 5 channel multiple peak monitoring (MPM) device was used. The mass spectrometer was coupled to a Carlo-Erba Gas chromatograph. The gas chromatograph was equipped with an SE-54 fused silica capillary column (0.25 mm x 30 m) which was coupled directly with the ion source.

B. Gas Chromatographic Conditions

Typical operating conditions were: Helium with a linear velocity of 35 cm/sec, injector 250°C, detector 275°C. For TCDD and TCDF the GC parameters were: column temperature 150°C (initial), and then programmed at 5/min to 280°C.

C. Mass Spectrometric Conditions and Multiple Ion Selection

The mass spectrometer was operated in the EI mode (70eV, 250°C) at 7500 resolving power. Peak profiles were acquired at an amplifier bandwidth of 30,000Hz. For the TCDD analysis, the ions m/z 319.8965, m/z 321.8936 and m/z 333.9339 (^{13}C-2, 3, 7, 8-TCDD) were monitored on three channels using the MPM. The instrument was tuned using m/z 330.9792 of PFK, and this ion was used as a check mass on channel 4. For the TCDF analysis, m/z 303.9016, m/z 305.8986 and m/z 333.9339 were monitored on 3 channels of the MPM. The instrument was tuned using the PFK m/z 304.9824 which was used as a check mass. The output of the mass spectrometer was recorded on a 3-pen strip chart recorder (Linear Model-595).

D. Calculation of Results

Quantification was achieved using the internal standard ratio method. Throughout the experiment, standard samples containing 2, 3, 7, 8-TCDD or 2, 3, 7, 8-TCDF and ^{13}C-2, 3, 7, 8-TCDD were analyzed. The slopes of the calibration plots were taken as the averages of the ratios of $(I^{334}/ng)/(I^{322}/ng)$. (I is the normalized intensity for the designated mass) for TCDD and $(I^{334}/ng)/(I^{306}/ng)$ for TCDF obtained using the standard samples.

Residues of TCDD or TCDF in actual samples were calculated by comparing the ratios of intensities of I^{322}/I^{334} (for TCDD) and I^{306}/I^{334} (for TCDF) obtained for a given sample with the slope of the calibration plot. The detection limit was considered to be the respective value obtained for an intensity of 2.5 x noise level measured at the base line.

The internal standard (^{13}C-2, 3, 7, 8-TCDD) was utilized in the calculation of percent recoveries, and in doing so the absolute intensity (I^{334} normalized) was measured and compared with the intensities (I^{334}/ng) obtained by injecting standard solutions of the internal standard. The recovery for TCDF was assumed to be identical to that for TCDD according to this calculation method.

Table 1-A. Verification of Solvent for Soxhlet Extraction of XAD and Florisil

Sample/Solvent	Spike Level (ng)			Percent Recovery of		
	2378-TCDD	2378-TCDF	^{13}C-2378-TCDD	2378-TCDD	2378-TCDF	^{13}C-2378-TC
XAD/Hexane	2.95	2.96	2.9	90	65	80
XAD/10% Benzene in Hexane	3.10	2.9	3.1	80	60	75
XAD/20% Benzene in Hexane	3.0	2.9	3.1	80	55	75
XAD/20% Benzene in Hexane			3.2	nd	nd	60
Florisil/Hexane	3.05	2.84	3.0	55	50	50
Florisil/10% Benzene in Hexane	3.10	2.84	3.0	80	75	75
Florisil/20% Benzene in Hexane	3.05	2.84	3.0	35	55	55
Florisil/20% Benzene in Hexane			3.0	nd	nd	70

nd - none detected

Table 2. TCDD in Emission Samples: Results of the Analysis of XAD Resin

Sample ID	C^{13} Level (ng)	Total Concentration of TCDD(ng)	Detection Limit (ng)	Percent Recovery	320/322 Isotope Ratio	Percentage of 2378-isomer
TRW 4061	10	nd[a]	.18	70		
TRW 4097	10	nd	.06	65		
TRW 4109	10	nd	.09	45		
TRW 4115	10	nd	.08	70		
TRW 4132	8.13	1.5 ± .1[b]	.16	70	.74	100%
TRW 4133	10	3.4 ± .05[b]	.21	70	.79	100%

a - none detected

b - 3 determinants

Table 3. TCDF is Emission Samples: Results of the Analysis of XAD Resin

Sample ID	C^{13} Level (ng)	Total Concentration of TCDF (ng)	Detection Limit (ng)	Percent Recovery	320/322 Isotope Ratio	Percentage[b] of 2378-isomer
TRW 4061	10	nd[a]	.19	70		
TRW 4097	10	nd	.28	65		
TRW 4109[c]	10	nd	.68	45		
TRW 4115	10	nd	.08	70		
TRW 4132	8.13	1.0	.60	70	.79	100%
TRW 4133	10	1.7	.20	70	.83	100%

a - none detected

b - Maximum possible concentrations of the 2,3,7,8-TCDF isomer is given. The determination was based on the signal that had a relative retention time identical to authentic 2378-TCDF on an SE-54 fused silica capillary column.

c - TRW 4109; none detected by capillary column GC/HRMS at a detection limit of .04ng.

Table 4. TCDD in Emission Samples: Results of the Analysis of Florisil

Sample ID	C^{13} Level (ng)	Total Concentration of TCDD (ng).	Detection Limit (ng)	Percent Recovery	320/322 Isotope Ratio	Percentage of 2378-isomer
TRW 4062	10	nd[a]	.13	80		
TRW 4068	10	nd	.19	45		
TRW 4080	10	nd	.07	70		
TRW 4092	10	nd	.11	50		
TRW 4098	10	nd	.05	80		
TRW 4104	10	nd	.18	60		
TRW 4110	10	nd	.07	60		
TRW 4116	10	nd	.04	100+		
TRW 4130	7.88	$(2.7 \pm .2)^b$	.19	40	.77	100%
TRW 4131	7.88	1.5	.18	45	.88	100%

a - none detected

b - 3 determinants

Table 5. TCDF in Emission Samples: Results of the Analysis of Florisil

Sample ID	C^{13} Level (ng)	Total Concentration of TCDF (ng)	Detection Limit (ng)	Percent Recovery	320/322 Isotope Ratio	Percentage of 2378-Isomer
TRW 4062	10	2.1	.13	80	.82	27
TRW 4068	10	nd[a]	.26	45		
TRW 4080[c]	10	nd	.25	70		
TRW 4092	10	1.0	.24	50	.82	
TRW 4098	10	.37	.14	80	.71	20
TRW 4104[d]	10	nd	.28	60		
TRW 4110	10	.12	.12	60	.87	
TRW 4116	10	nd	.12	100+		
TRW 4130	7.88	1.3	.20	40	.83	100
TRW 4131	7.88	1.5 ± .4 (e)	.34	45	.85	100

a - none detected

b - Maximum possible concentrations of the 2,3,7,8-TCDF isomer is given. The determination was based on the signal that had a relative retention time identical to authentic 2378-TCDF on an SE-54 fused silica capillary column.

c - TRW 4080: .16 ng of total TCDF was detected by capillary GC/HRMS at a detection limit of .08 ng

d - TRW 4104: .28ng of total TCDF was detected by capillary GC/HRMS at a detection limit of 0.28ng.

e - Two determinants

Table 6. TCDD in Emission Samples: Results of the Analysis of Probe Rinses and Impingers

Sample ID	C^{13} Level (ng)	Total Concentration of TCDD (ng)	Detection Limit (ng)	Percent Recovery	320/322 Isotope Ratio	[illegible]centage of 2378-isomer
TRW 4057, 4058	20	nd[a]	.21	45		
TRW 4063, 4064	20	nd	.46	45		
TRW 4075, 4076	20	nd	.13	30		
TRW 4087, 4088	20	nd	.09	65		
TRW 4093, 4094	20	nd	.08	85		
TRW 4099, 4100	20	nd	.16	70		
TRW 4105, 4106	20	nd	.53	50		
TRW 4111 (Probe Rinse)	10	nd	.11	100+		
TRW 4112 (Impinger)	10	nd	.12	100+		
TRW 4124, 4125	10	3.4	.15	55	.81	100%
TRW 4126, 4127	10	2.0	.17	50	.81	100%
TRW 4128, 4129	10	4.0	.22	50	.82	100%
TRW 4138, 4139 (Blank)	nd					

a - none detected

Table 7. TCDF in Emission Samples: Results of the Analysis of the Probe Rinses and Impingers

Sample ID	C^{13} Level (ng)	Total Concentration of TCDF (ng)	Detection Limit (ng)	Percent Recovery	320/322 Isotope Ratio	Percentage of 2378-isomer[b]
TRW 4057, 4058	20	nd[c]	1.0	45		
TRW 4063, 4064	20	nd	.28	45		
TRW 4075, 4076[d]	20	nd	.27	30		
TRW 4087, 4088	20	nd	.44	65		
TRW 4093, 4094	20	nd[a]	.38	85		
TRW 4099, 4100	20	nd	.12	70		
TRW 4105, 4106	20	nd	.45	50		
TRW 4111 (Probe Rinse)	10	nd	.11	100+		
TRW 4112 (Impingers)	10	nd	.10	100+		
TRW 4124, 4125	10	3.4	.13	55	.80	100%
TRW 4126, 4127	10	1.7	.20	50	.84	100%
TRW 4128, 4129	10	3.5 ± .4	.33	50	.80	100%
TRW 4138, 4139 (Blank)	nd					

a - none detected

b - Maximum possible concentrations of the 2,3,7,8-TCDF isomer is given. The determination was based on the signal that had a relative retention time identical to authentic 2378-TCDF on an SE-54 fused silica capillary column.

c - TRW 4057, 4058: .49ng of total TCDF was detected by capillary GC/HRMS at a detection limit of .10ng.

d - TRW 4075, 4076: .18ng of total TCDF was detected by capillary GC/HRMS at a detection limit of .09ng.

e - Two determinants

Table 8. TCDD in Chemical Waste Samples (Revised).

Sample ID	C^{13} Level (ng)	Sample Weight (g)	Total Concentration of TCDD (ppb)	Detection Limit (ppb)	Percent Recovery	320/322 Isotope Ratio	Percentage of 2378-TCDD Isomer
TRW 4016	30	.60	nd	1	55		
TRW 4017	30	.50	nd	1	80		
TRW 4020	30	.60	nd	2	45.		
TRW 4021	30	.60	nd	1	75		
TRW 4022	30	.65	nd	2	35		
TRW 4023	30	.60	nd	1	55		
TRW 4134	27	.39	75	5	40	.75	100
TRW 4135	27	.50	nd[a]	5	45	.63	
TRW 4136	27	.42	105	20	40	.77	100
TRW 4137	27	.51	nd[b]	5	45	.73	

(a) 1.2 ppb of TCDD was detected at a detection limit of 0.5ppb by capillary GC/HRMS

(b) 1.3 ppb of TCDD was detected at a detection limit of .7 ppb by capillary GC/HRMS

For TRW 4016 to TRW 4023, the data presented were obtained by capillary column GC/HRMS.

For TRW 4134 to TRW 4136 packed column GC/HRMS data are presetned unless otherwise indicated.

Table 9. TCDF Concentration in Chemical Waste (Revised)

Sample ID	C^{13} Level (ng)	Sample Weight (g)	Total Concentration of TCDF (ppb)	Detection Limit(ppb)	Percent Recovery	320/322 Isotope Ratio	Percentage of 2378-TCDF Isomer
TRW 4016	30	.60	25	.5	55	.66	40
TRW 4017	30	.50	40	1.0	80	.74	50
TRW 4020	30	.60	25	1.0	45	.79	50
TRW 4021	30	.60	15	.5	75	.70	60
TRW 4022	30	.65	25	.5	35	.75	40
TRW 4023	30	.60	35	1.0	55	.78	50
TRW 4134	27	.39	115	20	40	.79	
TRW 4135	27	.50	25	5	45	.78	
TRW 4136	27	.42	165	20	40	.76	
TRW 4137	27	.51	20	10	45	.79	

For TRW 4016 to 4023, the data presented were obtained by capillary column GC/HRMS.

For TRW 4134 to 4137 packed column GC/HRMS analysis data are presented.

Table 10. Relative Retention Times[a] of the TCDF Isomers Present in Emission Samples

Sample ID	No. of Isomers	Relative Retention Time										
		D[b]1	D2	D3	D4	D5	D6	D7	D8	D9	D10	D11
TRW 4062	7	.900	.916	.932		.945			.967	.980	1.000	1.016
TRW 4080	1										1.000	
TRW 4092	5		.915	.932	.942	.946					1.000	
TRW 4098	5		.917			.946			.968	.980	1.000	
TRW 4104	1										1.000	
TRW 4110	2									.978	1.000	
TRW 4057 and 4058	2									.978	1.000	
TRW 4075 and 4076	1										1.000	

(a) Retention times relative to authentic 2,3,7,8-TCDF. An SE-54 (.25 x 30m) fused silica column was used for the above analysis.

(b) The numbers D1 - D11 are arbitrary numbers given for comparison purposes.

Table 11. Relative Retention Times(a) of the TCDF Isomers Present in Chemical Waste Samples

Sample ID	No. of Isomers	Relative Retention Times										
		D5	D6	D7	D8	D9	D10	D11	D12	D13	D14	D15
TRW 4016(b)	4						1.000	1.017	1.067	1.073		
TRW 4017(b)	3						1.000	1.016	1.067			
TRW 4020(b)	3						1.000	1.016	1.065			
TRW 4021(b)	4						1.000	1.017		1.073	1.083	
TRW 4022(b)	3						1.000	1.016	1.067			
TRW 4023(b)	3						1.000	1.016	1.067			
PCR Waste	8	.946	.954	.962	.971		1.000	1.016			1.083	1.091

(a) Retention time relative to authentic 2,3,7,8-TCDF. An SF-54 (.25 X 30m) fused silica column was used for the above analysis.

(b) The percent recoveries of TCDF in these samples ranged from 10 to 30%.

(c) The reextracts of chemical wastes were analyzed by SP-2330 fused silica column (see Table 12).

Table 12. Relative Retention Times(a) of the TCDF Isomers Present in Chemical Waste

Sample ID	No. of Isomers	Relative Retention Time						
		1	2	3	4	5	6	7
TRW 4016	6	.975	1.000		1.034	1.046	1.110	1.163
TRW 4017	6	.975	1.000	1.028	1.037		1.109	1.159
TRW 4020	7	.975	1.000	1.028	1.034	1.046	1.110	1.154
TRW 4021	7	.975	1.000	1.028	1.035	1.044	1.109	1.159
TRW 4022	6	.975	1.000		1.034	1.044	1.109	1.159
TRW 4023	6	.975	1.000		1.032	1.044	1.109	1.161

(a) The retention time is relative to authentic 2,3,7,8-TCDF. An SP-2330 (.24 x 30m) fused silica column was used for the above analysis.

APPENDIX I

RESEARCH TRIANGLE INSTITUTE REPORT ON QUALITY ASSURANCE EFFORT ON THE ANALYSES OF AUDIT SAMPLES FOR PCBS

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
INDUSTRIAL ENVIRONMENTAL RESEARCH LABORATORY
RESEARCH TRIANGLE PARK
NORTH CAROLINA 27711

March 2, 1983

SUBJECT: Performance Audit -- Evaluation of TRW Analyses of PCB Performance Audit Samples for the At-Sea Incineration of PCB Wastes on the M/T VULCANUS

FROM: Gary L. Johnson
Quality Assurance Officer (MD-62)

TO: Merrill Jackson
Technical Support Staff, IERL-RTP (MD-62)

The attached report details the evaluation by Research Triangle Institute of TRW's analyses of 12 audit samples supplied to TRW as part of the quality assurance assistance on the At-Sea Incineration Project last September.

The results of the audit appear to indicate that TRW's analyses of the audit samples were acceptable within what is considered to be reasonable precision and accuracy for the determination of PCBs. This conclusion was reached irrespective of the actual destruction efficiencies (DEs) calculated by TRW for the test burns and is a consensus of the RTI, TRW, and EPA reviewers of the QA data.

If you have any questions about the audits, please let me know.

Attachment

cc: J. A. Dorsey
J. S. Ford

EVALUATION OF TRW ANALYSES OF PCB PERFORMANCE AUDIT SAMPLES

INTRODUCTION

During August 1982, TRW at Research Triangle Park, NC, sampled gaseous and particulate source emissions from shipboard liquid incinerators onboard the M/T Vulcanus as part of monitoring of the incineration of PCB-contaminated oils. The emission samples were collected using a PCB sampling train and were recovered by solvent extraction and analyzed by gas chromatography/electron capture detection (GC/ECD) and gas chromatography/mass spectrometry (GC/MS). The protocol is described in the September 1982 Draft Analysis Plan for the At-Sea Incineration of PCB Wastes Onboard the M/T Vulcanus (included here as Appendix A), henceforth the "Analysis Protocol."

At the request of the IERL quality assurance (QA) officer, RTI submitted comments on the protocol (Appendix B) and prepared 12 performance evaluation audit samples to test TRW's application of the protocol. Correspondence with TRW concerning how the audit samples were to be analyzed is included in Appendix C.

SAMPLE SELECTION AND PREPARATION

Twelve audit samples were prepared and submitted to TRW for analysis. The composition of these samples is given in Table 1. Sample 9 was prepared from standard isomers obtained from Ultra Scientific, Inc. Sample 10, an oil containing Aroclor 1254, was obtained from Supelco. Sample 11 was an aliquot of the solvent (toluene) used to prepare the samples. All other samples were prepared by appropriate dilution of Aroclor standards obtained from the EPA-EMSL-Cincinnati repository.

Samples 1, 2, 3, 4, 7, and 8 were to be spiked onto Florisil and/or cleaned up prior to analysis. Samples 5, 6, 11, and 12 were to be analyzed directly without cleanup. The waste oil, sample 10, was to be analyzed according to the same procedure TRW followed in analyzing waste feed oil collected from the Vulcanus.

Samples 3, 4, 5, and 12 were identical as were Samples 1 and 2 and Samples 6, 7, and 8. These three solutions consisted of various amounts of the three PCB Aroclors, 1016, 1254, and 1260. Samples 6, 7, and 8 contained, in addition, a mixture of pesticides to test for interference with PCB quantitation. Sample 9 was a more challenging sample consisting of eight PCB isomers covering a wide concentration range. This sample's atypical combination of isomers is probably more representative of thermally altered PCBs than the easily recognized patterns of the PCB Aroclor mixtures in the other samples.

EVALUATION OF TRW ANALYSIS RESULTS

TRW subcontracted the GC/MS analyses of the 12 audit samples. Three samples were not analyzed by the GC/MS subcontractor for reasons given later in this section. TRW analyzed 11 of the 12 samples by GC/ECD. GC/ECD data were provided to RTI after the February 7, 1983, meeting.

TRW's reported results for both GC/MS and GC/ECD analyses of the audit samples are shown in Tables 2 and 3 and are compared with the expected results in Tables 4 and 5. Copies of the analysis reports submitted by TRW are given in Appendix D.

Florisil-Spiked Samples

Samples 1, 2, 3, 4, 7, and 8 were to be spiked onto Florisil prior to analysis. Florisil is commonly used in PCB work to remove interfering organics prior to the analysis step (GC/ECD or GC/MS). Samples 7 and 8 contained potentially interfering substances that the Florisil should have removed. Samples 1, 2, 3, and 4 could just as easily have been analyzed directly.

The results for the samples subjected to Florisil cleanup were 15 to 30 percent lower than expected.

TRW stated in their report that Samples 1 and 2 were too low in concentration to be analyzed by GC/MS. They arrived at this conclusion after direct analysis of the samples by GC/ECD, which was not called for in the instructions included with the audit samples. As discussed in Appendix C, it would have been possible for TRW to have spiked Samples 1 and 2 and quantitated the resulting extracts had the extracts been reduced in volume to 0.1 mL as called for in the Analysis Protocol. TRW's response was as follows:

> The analysis protocol stated that sample concentration to less than 1 mL would be performed if necessary. However, a final sample volume of 4 mL was determined to be adequate to achieve the desired minimum detectable level (MDL). Based on information supplied by RTI at the time QCs 1 & 2 were delivered [i.e., the samples contained between 50 and 200 pg/μL (stated MDL) in 100 μL], these samples were determined to have been below the MDL in 4 mL. Therefore, these samples were not analyzed by GC/HRMS, but were screened by GC/ECD. Based on this information, RTI submitted samples 3 & 4 for column cleanup and analysis.

Further discussion of this issue produced two additional pieces of information.

- The analytical protocols were not necessarily to be followed verbatim. Modifications could be made so long as they did not compromise the resulting data quality. TRW's decision not to reduce the sample extract volume below 0.4 mL was therefore acceptable in light of this.
- The GC/ECD results for Samples 1 and 2 were commensurate with the GC/MS and GC/ECD results for the other Florisil-spiked samples.

Direct Analysis Samples

The GC/MS biases for the direct analysis samples 5, 6, 9, 11, and 12 were generally two times those for the Florisil-spiked samples. Samples 5 and 12, identical to Florisil-spiked Samples 3 and 4, were 53 percent and 39 percent lower than expected. The GC/ECD results were in general agreement with the GC/MS and GC/ECD results for the Florisil-spiked samples.

That the GC/MS-analyzed Florisil-spiked sample biases are positive relative to the direct analysis sample biases suggests that some material on the Florisil could have been extracted and quantitated as PCBs. However, the GC/ECD biases for these same samples do not confirm this.

Sample 9, the most complicated and probably most realistic of the synthetically prepared audit samples, was initially reported by TRW to contain nearly three times the expected concentration of PCBs. This was later determined to be due to a factor of 10 calculation error in the quantitation of the 3-chlorobiphenyl. Documentation for this was provided by TRW and is given in Appendix D. The corrected GC/MS result was 12 percent higher than expected. No GC/ECD data on this sample were available.

Sample 11, the unspiked toluene diluent, was reported by TRW, as expected, to contain no detectable PCBs.

Sample 10, PCBs in transformer oil, was not analyzed by GC/MS. TRW's response was as follows:

> As stated in the analysis protocol..., the raw waste was to be cleaned and analyzed as necessary. The high levels of PCBs in the raw waste [from the Vulcanus] (20-30%) required dilutions only (10,000 fold for GC/HRMS and 25,000 fold for GC/MS) to accomplish analysis, thereby eliminating any hydrocarbon interferences particularly troublesome to MS procedures. A GC/ECD screen of sample 10 revealed PCB levels to be only a few hundred ppm. This sample could have been analyzed by GC/HRMS, but only after extensive cleanup to remove hydrocarbon interferences. Such a procedure could have been performed, but would most certainly have been different from the procedures utilized for the "real" raw waste samples. A transformer oil with only a few hundred ppm of PCBs hardly represents a true waste sample.

RTI was not informed of the above facts until the February 7, 1983, meeting. Thus, even though the GC/ECD analysis of Sample 10 showed a bias of only -20 percent, this result is not necessarily indicative of performance on waste samples.

The precision of the GC/MS and GC/ECD analyses of the duplicate pairs 3 and 4, 7 and 8, and 5 and 12 expressed as relative percent difference was quite good and ranged from 1 to 13 percent (Table 5).

TABLE 1. AUDIT SAMPLE COMPOSITION

Sample number	Composition	Concentration	Total concentration	Total mass	Analysis requested
1 and 2	Aroclor 1016 Aroclor 1254 Aroclor 1260	625 pg/μL 500 pg/μL 250 pg/μL	1.37 ng/μL	137.5 ng	Florisil cleanup & analysis
3 and 4	Aroclor 1016 Aroclor 1254 Aroclor 1260	62.5 ng/μL 50.0 ng/μL 25.0 ng/μL	137.5 ng/μL	13.750 μg	Florisil cleanup & analysis
5	Aroclor 1016 Aroclor 1254 Aroclor 1260	62.5 ng/μL 50.0 ng/μL 25.0 ng/μL	137.5 ng/uL	--	Direct analysis
6	Aroclor 1016 Aroclor 1254 Aroclor 1260 Pesticide mixture	55.6 ng/μL 44.4 ng/μL 22.2 ng/μL 11.1 ng/μL	122.2 ng/μL 133.0 ng/μL	--	Direct analysis
7 and 8	Aroclor 1016 Aroclor 1254 Aroclor 1260 Pesticide mixture	55.6 ng/μL 44.4 ng/μL 22.2 ng/μL 11.1 ng/μL	122.2 ng/μL 133.0 ng/μL	12.22 μg	Florisil cleanup & analysis

(continued)

TABLE 1 (continued)

Sample number	Composition	Concentration	Total concentration	Total mass	Analysis requested
9	3-chlorobiphenyl	2,002 ng/mL			
	2,5-dichlorobiphenyl	66.7 ng/mL			
	3,5-dichlorobiphenyl	133 ng/mL			
	2,2',4,4',6,6'-hexachlorobiphenyl	54.1 ng/mL			
	2,2',3,4,4',5-hexachlorobiphenyl	1.41 ng/mL			
	2,2',3,4,4',5,-6,6'-octachlorobiphenyl	38.4 ng/mL			
	2,2',3,4,5',6-hexachlorobiphenyl	4,207 ng/mL			
			6.503 ng/µL	--	Direct analysis
10	Aroclor 1254 in Diala AX oil	500 µg/g	--	--	As called for in protocol
11	Unspiked toluene	--	--	--	Direct analysis
12	Aroclor 1016	62.5 ng/µL			
	Aroclor 1254	50.0 ng/µL			
	Aroclor 1260	25.0 ng/µL			
			137.5 ng/µL		Direct analysis

TABLE 2. CONCENTRATION OF PCBS IN RTI QUALITY CONTROL (QC) SAMPLES BY GC/MS BY CHLORINE ISOMER GROUP[a]

QC #	Cl_1	Cl_2	Cl_3	Cl_4	Cl_5	Cl_6	Cl_7	Cl_8	Cl_9	Cl_{10}	TBB % recoveries	Units	Sample type	Sample volume
1[b]	-	-	-	-	-	-	-	-	-	-	NA	mg	Direct analysis[c]	0.4 mL
2[b]	-	-	-	-	-	-	-	-	-	-	NA	mg	Direct analysis[c]	0.4 mL
3	53.1	827	3,099	2,691	2,107	2,059	133	ND	ND	ND	105	mg	Flor. ext.	4 mL
4	53.1	718	3,085	2,667	2,105	2,057	131	ND	ND	ND	107	mg	Flor. ext.	4 mL
5	0.192	3.52	12.76	14.31	13.47	14.16	5.96	0.236	ND	ND	NA	ng/µL	Direct analysis	As received
6	0.190	3.50	12.53	15.7	16.5	16.04	5.36	0.15	ND	ND	NA	ng/µL	Direct analysis	As received
7	57.5	540	2,331	2,068	1,778	1,461	144	ND	ND	ND	97	mg	Alumina C-U	4 mL
8	75.3	679	3,032	2,538	1,917	1,071	178	ND	ND	ND	111	mg	Alumina C-U	4 mL
9	20.3	0.11	ND	0.16	0.06	4.95	ND	ND	ND	ND	NA	ng/µL	Direct analysis	As received
10[b]	-	-	-	-	-	-	-	-	-	-	NA	ng/µL	Direct analysis[c]	As received
11	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	NA	ng/µL	Direct analysis	As received
12	0.36	3.64	16.5	19.07	20.2	18.6	5.77	0.26	ND	ND	NA	ng/µL	Direct analysis	As received

NA = Not applicable.

ND = Not detected.

[a] Verbatim report from TRW.

[b] Not analyzed; QC 1 and 2 were too low in concentration; QC 10 required cleanup due to apparent presence of mineral oil carrier for PCB.

[c] Not analyzed as called for.

TABLE 3. CONCENTRATION OF PCBs IN QA SAMPLES BY GC/ECD BY CHLORINE ISOMER GROUP

QA #	Cl_1	Cl_2	Cl_3	Cl_4	Cl_5	Cl_6	Cl_7	Cl_8	Cl_9	Cl_{10}	Aroclor		Units	Sample Type	Sample Volume
											1254	1260			
1	ND[1]	12.1	27.7	53.7	46.8	42.7	6.93	0.62	ND	ND	50	40	ng	Direct Analysis	0.4 mL
2	ND	8.88	9.53	45.6	22.7	20.7	5.61	0.97	ND	ND	34.8	57.7	ng	Direct Analysis	0.4 mL
3	ND	656	1708	3388	2292	1822	239	32.6	ND	ND	4054	2346	ng	Flor. Ext.	4 mL
4	ND	632	2032	2448	2312	1832	230	35.3	ND	ND	3037	2328	ng	Flor. Ext.	4 mL
5	ND	9.50	20.1	35.4	24.1	19.2	2.60	0.370	ND	ND	37.3	23.2	ng/µL	Direct Analysis	As Received
6	ND	2.99	14.2	27.3	16.0	14.4	2.13	0.295	ND	ND	28.7	10.9	ng/µL	Direct Analysis	As Received
7	ND	831	1435	2704	2004	1320	212	26.6	ND	ND	3548	2020	ng	Alumina C-U[2]	4 mL
8	ND	752	1276	2508	1632	1680	215	33.2	ND	ND	3042	1763	ng	Alumina C-U	4 mL
9	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ng/µL	Direct Analysis	As Received
10	ND	3.33	2.65	101	134	141	3.57	0.22	ND	ND	399	ND	ng/µL	Direct Analysis	As Received
11	ND	ND	0.001	0.004	0.007	0.010	0.001	0.003	ND	ND	0.013	0.013	ng/µL	Direct Analysis	As Received
12	ND	10.2	16.6	30.7	20.0	21.7	2.58	0.346	ND	ND	34.7	21.4	ng/µL	Direct Analysis	As Received

[1] ND = Not Detected.
[2] C-U = Clean-Up.

TABLE 4. COMPARISON OF TRW ANALYSIS RESULTS WITH EXPECTED VALUES

	Expected value[a]	TRW value[b]		Percent bias[c]	
		GC/MS	GC/ECD	GC/MS	GC/ECD
Florisil-spiked samples (ng)					
1	137.5	NA	191	--	+39
2	137.5	NA	114	--	-17
3	13,750	10,969	10,138	-20	-26
4	13,750	10,816	9,521	-21	-31
7	12,222	8,380	8,533	-31	-30
8	12,222	10,290	8,096	-16	-34
Direct analysis samples (ng/µL)					
5	137.5	64.6	111	-53	-19
12	137.5	84.3	110	-39	-20
6	122.2	70.0	77.3	-43	-37
9[d]	6.50	25.6	NQ	+294	--
9[e]	6.50	7.26	NQ	+11.9	--
11	0	ND	ND	0	0
Waste oil sample (ng/µL)					
10	500	NA	399	--	-20

NA = Not analyzed.

ND = Not detected.

NQ = Not quantitated at this time.

[a] Sum of all PCBs as Aroclor in the sample.

[b] Sum of all PCBs as chlorine isomer group (Cl_1-Cl_{10}).

[c] Percent bias = $\frac{\text{TRW value - expected value}}{\text{expected value}} \times 100\%$.

[d] Before correction for calculation error (see text).

[e] After correction for calculation error.

TABLE 5. PRECISION OF TRW ANALYSES OF BLIND DUPLICATES

	TRW value[a]		Relative percent difference[b]	
	GC/MS	GC/ECD	GC/MS	GC/ECD
Florisil-spiked samples (ng)				
3	10,969	10,138		
4	10,816	9,521	0.7	3.1
7	8,380	8,533		
8	10,290	8,096	10.2	2.6
Direct analysis samples (ng/μL)				
5	64.6	111		
12	84.3	110	13	0.5

[a] Sum of all PCBs as chlorine isomer group (Cl_1-Cl_{10}).

[b] Relative % difference = $\frac{x_1 - x_2}{x_1 + x_2} \times 100\%$.

DISCUSSION OF RESULTS

Accuracy of Standards and Comparability of Results

The quantitation of PCBs as individual isomers or isomer groups or as Aroclors is highly dependent on the availability of standards of known composition and concentration. TRW, in their letter of February 7, 1983, expressed concern that the audit sample expected results based on total PCBs as Aroclor could not be compared with the TRW reported results which were based on PCBs as isomer groups. Their comments were as follows:

> The GC/ECD analysis of the audit samples for Aroclors are in excellent agreement with the values reported by RTI. The comparison of the TRW, GC/HRMS results with the RTI values in Table 3 cannot be accepted as a valid approach, even though the results are favorable. The TRW values are based on individual determination of each chlorine isomer group, whereas the RTI values are based on a total concentration as Aroclor which have presumably been verified by analyses performed in RTI laboratories. Although Aroclor patterns are generally identifiable from one standard to the next, it is well known that the amount of any one isomer may vary from one standard to the next. Commercially available Aroclor standards have been found to vary as much as 50% from one lot to the next. TRW would like to see the results of RTI's analysis of the individual PCB isomer groups in order for a valid and realistic comparison to be made. This is the necessary approach as the D.E.s are presented by isomer group. Note: This is important in that the D.E.s were calculated by isomer group for final calculation.
>
> The fact that the TRW standards were prepared from 99% pure individual PCB isomers, and that the bias is consistently negative, suggests that the EMSL-Cincinnati values may be in error.

These are not valid concerns for several reasons. First, the audit samples in question were prepared from Quality Assurance Technical Materials obtained from the EPA-EMSL-Cincinnati repository. From discussions with EMSL-Cincinnati, RTI learned that the individual Aroclor standards prepared by the EMSL contractor were obtained commercially as the Aroclor, made up gravimetrically in methanol and subjected to interlaboratory testing to verify the gravimetric value. The gravimetric values of the standards used for audit sample preparation agreed with the interlaboratory results within 5 percent. However, the value reported by EMSL-Ci is based on the gravimetric concentration and not the analyzed result. Thus, there should be little question about the accuracy of the audit sample standards.

With respect to TRW's concern that their results are based on isomer group concentration and not total Aroclor concentration it should be stated that the fact that they are performing individual isomer determinations will allow them to quantitate any Aroclor or mixture of isomers giving total PCBs as the sum of individual isomers. Thus, it is not necessary for RTI to provide an analysis of the individual PCB isomer groups since the audit sample results were compared on the basis of total PCBs.

Comparability of GC/MS and GC/ECD Results for Audit Samples and Waste Samples

TRW, in their February 7, 1983, letter, states that the close agreement between the GC/MS and the GC/ECD analyses of the audit samples and the raw waste support the validity of the destruction and removal efficiencies. However, a comparison of the GC/MS and GC/ECD data for both total PCBs and isomer groups shows large (> 40%) differences for more than one-third of all the isomer groups in the waste and audit samples (Table 7) and for more than half of the total PCBs reported in the waste samples (Table 6).

In Waste Sample 4016 (Table 7) all isomers were 50 to 80 percent lower by GC/ECD when referenced to the GC/MS value. In the other waste samples the heptachlorbiphenyls were consistently 60 to 70 percent lower by GC/ECD. Much of the difference in reported concentrations in the waste samples by GC/MS and GC/ECD can be attributed to the differences in results for the heptachlorobiphenyls. A similar trend was observed for the pentachlorobiphenyls. The dichlorobiphenyls were typically 50 percent greater by GC/ECD than by GC/MS.

Heptachlorobiphenyl concentrations by GC/MS and GC/ECD also varied considerably in all of the audit samples with negative differences of greater than 50 percent observed for more than half of the samples. These differences did not significantly affect the total PCBs reported because the heptachlorobiphenyls were a minor constituent of the audit samples. Other isomer group concentrations varied widely between the two methods.

RECOMMENDATIONS

Reasons for these differences are not obvious. However, there are several possible explanations for the differences between the methods as well as some of the differences between the reported and expected results. The use of a single response factor obtained by averaging the responses of three separate isomers for each chlorine isomer group rather than quantitation based on responses of a separate isomer standard for each isomer identified could be responsible for some of the errors and differences noted. Although it is difficult to obtain some of the specific isomers, their use in future such analyses may reduce the analytical error significantly. The use of an alternate GC column may preclude errors from coeluting PCBs. The same column was used for both the GC/MS and GC/ECD analyses performed by TRW.

TABLE 6. COMPARISON OF TOTAL PCBs IN RAW WASTE AND RTI QA SAMPLES BY GC/MS AND GC/ECD

Waste (g/L)	Total PCBs GC/MS	Total PCBs GC/ECD	Percent bias
4016	283	77.2	-73
4017	352	293	-17
4020	345	265	-23
4021	267	168	-37
4022	352	200	-43
4023	314	181	-42
QA samples			
3 (ng)	10,969	10,138	-8
4 (ng)	10,816	9,521	-12
5 (ng/μL)	64.6	111	+72
6 (ng/μL)	70	77.3	+10
7 (ng)	8,380	8,533	+2
8 (ng)	10,290	8,096	-21
12 (ng/μL)	84.3	110	+30

$$\% \text{ bias} = \frac{\text{GC/ECD value} - \text{GC/MS value}}{\text{GC/MS value}} \times 100\%.$$

TABLE 7. COMPARISON OF PCB ISOMER GROUPS IN RAW WASTE AND QA SAMPLES BY GC/MS AND GC/ECD

Waste (g/L)	Isomer group GC/MS	Isomer group GC/ECD	Percent bias
4016			
Cl_1	0.16	0	-
Cl_2	4.94	1.98	-60
Cl_3	20.0	5.77	-71
Cl_4	29.7	12.2	-59
Cl_5	41.7	10.9	-74
Cl_6	103.0	28.6	-72
Cl_7	69.5	12.0	-83
Cl_8	14.0	5.35	-62
Cl_9	0	0.38	-
Cl_{10}	0	0.045	-
Total	283	77.2	-73
4017			
Cl_1	0.19	0	-
Cl_2	5.27	7.68	+46
Cl_3	20.5	21.7	+6
Cl_4	30.4	44.4	+46
Cl_5	53.5	57.1	+7
Cl_6	113.0	103.0	-9
Cl_7	108.0	39.5	-63
Cl_8	21.5	17.9	-17
Cl_9	0	1.2	-
Cl_{10}	0	0.12	-
Total	352	293	-17
4020			
Cl_1	0	0	-
Cl_2	5.69	8.8	+55
Cl_3	27.5	25.7	-7
Cl_4	36.2	48.3	+33
Cl_5	49.5	34.6	-30
Cl_6	105.0	91.5	-13
Cl_7	98.8	37.6	-62
Cl_8	22.3	17.1	-23
Cl_9	0	1.07	-
Cl_{10}	0	0.172	-
Total	345	265	-23

(continued)

TABLE 7 (continued)

Waste (g/L)	Isomer group		Percent bias
	GC/MS	GC/ECD	
4021			
Cl_1	0	0	-
Cl_2	5.21	5.8	+11
Cl_3	21.6	17.7	-18
Cl_4	24.2	26.9	+11
Cl_5	38.6	20.5	-47
Cl_6	87.2	61.4	-30
Cl_7	79.0	22.3	-72
Cl_8	10.7	12.2	+14
Cl_9	0	0.675	-
Cl_{10}	0	0.157	-
Total	267	168	-37
4022			
Cl_1	0.28	0	-
Cl_2	3.28	5.88	+79
Cl_3	19.3	16.6	-14
Cl_4	31.2	33.0	+6
Cl_5	53.7	22.4	-58
Cl_6	114.0	75.6	-34
Cl_7	109.0	30.9	-72
Cl_8	21.7	14.1	-35
Cl_9	0	0.990	-
Cl_{10}	0	0.140	-
Total	352	200	-43
4023			
Cl_1	0	0	-
Cl_2	4.58	5.55	+21
Cl_3	16.0	15.4	-4
Cl_4	28.5	28.8	+1
Cl_5	49.7	24.7	-50
Cl_6	101.0	68.8	-32
Cl_7	92.0	25.8	-72
Cl_8	22.0	11.2	-49
Cl_9	0	0.217	-
Cl_{10}	0	0.083	-
Total	314	181	-42

(continued)

TABLE 7 (continued)

	Isomer group		
QA sample	GC/MS	GC/ECD	Percent bias
3 (ng)			
Cl_1	53.7	ND	-
Cl_2	827	656	-21
Cl_3	3,099	1,708	-45
Cl_4	2,691	3,388	+26
Cl_5	2,107	2,292	+9
Cl_6	2,059	1,822	-12
Cl_7	133	239	+80
Cl_8	ND	32.6	-
Cl_9	ND	ND	-
Cl_{10}	ND	ND	-
Total	10,969	10,138	-8
4 (ng)			
Cl_1	53.1	ND	-
Cl_2	718	632	-12
Cl_3	3,085	2,032	-34
Cl_4	2,667	2,448	-8
Cl_5	2,105	2,312	+10
Cl_6	2,057	1,832	-11
Cl_7	131	230	+75
Cl_8	ND	35.3	-
Cl_9	ND	ND	-
Cl_{10}	ND	ND	-
Total	10,316	10,138	-12
5 (ng/μL)			
Cl_1	0.192	ND	-
Cl_2	3.52	9.58	+172
Cl_3	12.76	20.1	+58
Cl_4	14.31	35.4	+147
Cl_5	13.47	24.1	+79
Cl_6	14.16	19.2	+36
Cl_7	5.96	2.6	-56
Cl_8	0.236	0.37	+57
Cl_9	ND	ND	-
Cl_{10}	ND	ND	-
Total	64.6	111	+72

(continued)

TABLE 7 (continued)

QA sample	Isomer group		Percent bias
	GC/MS	GC/ECD	
6 (ng/μL)			
Cl_1	0.19	ND	-
Cl_2	3.5	2.99	-15
Cl_3	12.53	14.2	+13
Cl_4	15.7	27.3	+74
Cl_5	16.5	16.0	-3
Cl_6	16.04	14.4	-10
Cl_7	5.36	2.13	-60
Cl_8	0.15	0.295	+97
Cl_9	ND	ND	-
Cl_{10}	ND	ND	-
Total	70	77.3	+10
7 (ng)			
Cl_1	57.5	ND	-
Cl_2	540	831	+54
Cl_3	2,331	1,435	-38
Cl_4	2,068	2,704	+31
Cl_5	1,778	2,004	+13
Cl_6	1,461	1,320	-10
Cl_7	144	212	-47
Cl_8	ND	26.6	-
Cl_9	ND	ND	-
Cl_{10}	ND	ND	-
Total	8,380	8,533	+2
8 (ng)			
Cl_1	75.3	ND	-
Cl_2	679	752	+11
Cl_3	3,032	1,276	-58
Cl_4	2,538	2,508	-1
Cl_5	1,917	1,632	-15
Cl_6	1,871	1,680	-10
Cl_7	178	215	-21
Cl_8	ND	33.2	-
Cl_9	ND	ND	-
Cl_{10}	ND	ND	-
Total	10,290	8,096	-21

(continued)

TABLE 7 (continued)

QA sample	Isomer group GC/MS	 GC/ECD	Percent bias
12 (ng/μL)			
Cl_1	0.36	ND	-
Cl_2	3.64	10.2	+180
Cl_3	16.5	16.6	+1
Cl_4	19.07	38.7	+103
Cl_5	20.2	20.0	-1
Cl_6	18.6	21.7	+17
Cl_7	5.77	2.58	-55
Cl_8	0.26	0.346	+33
Cl_9	ND	ND	-
Cl_{10}	ND	ND	-
Total	84.3	110	+30

APPENDIX I (A)

DRAFT ANALYSIS PLAN FOR THE AT-SEA INCINERATION OF PCB WASTES ONBOARD THE M/T VULCANUS

DRAFT

ANALYSIS PLAN FOR THE AT-SEA INCINERATION OF PCB-WASTES ONBOARD THE M/T VULCANUS

SEPTEMBER 1982

By

D. G. Ackerman, J. F. McGaughey, and D. E. Wagoner

TRW Inc.

Energy and Environmental Division
One Space Park, Redondo Beach, CA 90278

and

M. D. Jackson and L. Johnson

U.S. Environmental Protection Agency

Research Triangle Park, NC 27711

Contract No. 68-02-3174, Work Assignment No. 103

Task Officer: M. D. Jackson

Industrial Environmental Research Laboratory
Office of Environmental Engineering and Technology
Research Triangle Park, NC 27711

U.S. ENVIRONMENTAL PROTECTION AGENCY

Office of Research and Development
Washington, D.C. 20460

ANALYSIS PLAN FOR THE AT-SEA INCINERATION OF PCB-WASTESONBOARD THE M/T VULCANUS

1. Principle and Applicability

1.1 Principle. Gaseous and particulate Polychlorinated Biphenyls (PCBs) are withdrawn from the source using a sampling train. The PCBs are collected in the Florisil adsorbent tube and in the impingers in front of the adsorbent. The Florisil is followed by an XAD-2 trap and two basic impingers. The total PCBs in the train are determined by solvent extraction followed by Gas Chromatography/Electron Capture Detection (GC/ECD) and/or Gas Chromatography/Mass Spectroscopy (GC/MS).*

1.2 Applicability. This method is applicable to the determination of vaporous emissions from "shipboard liquid incinerators". The analysis of the samples should be conducted by chemical personnel experienced in determinations of trace organics utilizing sophisticated, instrumental techniques. All extract transfers should be made quantitatively by rinsing the apparatus at least three times with the appropriate solvent and adding the rinses to the receiving container. A pre-extracted boiling stone should be used in all evaporative steps to control "bumping".

2. Range and Minimum Detectable Limit (MDL)

The range of the analytical method may be expanded considerably through concentration and/or dilution. The total method sensitivity is also highly dependent on the volume of gases sampled. The MDL of the GC/ECD method is about 50 pg of total PCB's per 1 μL injection. The MDL of the GC/MS system ranges between 50-200 pg/μL.

---

* This document refers to the use of capillary columns for the separation of PCB isomers. Other columns may be used if they can be demonstrated to be adequate for the specific ______.

3. Interferences

Organochlorine compounds other than PCB, Tetrachlorodibenzofuran (TCDF) or Tetrachlorodibenzodioxin (TCDD) found in the raw waste may interfere with the analyses. Appropriate sample cleanup steps shall be performed as needed.

Throughout all stages of sample handling and analysis, care should be taken to avoid contact of samples and extracts with synthetic organic materials other than TFE® (polytetrafluorethylene). Adhesives should not be used to hold TFE® liners on lids, (but, if necessary, appropriate blanks must be run).

4. Precision and Accuracy

From sampling with identical and paired sampling trains, the precision of the method has been determined to be 10 to 15% of the PCB concentration measured. Recovery efficiencies on source samples spiked with PCB compounds ranged from 85 to 95% (Reference 1).

5. Apparatus

5.1 Gas Chromatograph. The gas chromatograph (GC) will be equipped with an electron capture detector (ECD) for the detection and quantitation of PCBs. The GC should also be equipped with a capillary column (such as a fused silica SE-54, 30 meter x 0.25 mm) capable of resolving the PCB isomers utilizing the appropriate temperature programming. The GC/ECD should be vented to a scrubber or vent for safety reasons. A compatible integrator should be used which has the ability to accurately integrate capillary peaks.

5.2 Gas Chromatograph/Mass Spectrometer/Data System. The gas chromatograph/mass spectrometer (GC/MS) should be equipped with a capillary column capable of resolving the PCB isomers. The MS system will have the capability of both total ion monitoring, as well as selective ion monitoring up to mass number 500.

5.3 Glassware

5.3.1 Soxhlet extractors - used for the extraction of the XAD-2 and Florisil adsorbents. Select the proper size Soxhlet to accomodate the volume of adsorbent.

5.3.2 Kuderna-Danish Evaporator - used to reduce the volume of solvent.

5.3.3 Separatory funnel - equipped with a Teflon stop-cock used for extraction of impinger solutions.

5.3.4 Miscellaneous volumetric glassware - used for determining the volume of solvent.

5.4 pH Meter. A pH meter equipped with appropriate glass and reference electrodes for measuring the pH of the collected samples.

5.5 Ion Chromatograph. An ion chromatograph equipped with the necessary columns and detectors required for the determination of chloride ion (Cl^-).

5.6 Glass Wool. Cleaned by thorough rinsing with hexane, dried in an oven at 110°C, and stored in a hexane-washed glass jar with TFE-lined screw caps.

6. Reagents and Chemicals

6.1 Solvents. Pesticide quality, Burdick and Jackson "Distilled in Glass" or equivalent, stored in original containers. A blank must be screened by the analytical detection method.

6.1.1 Acetone -

6.1.2 Hexane -

6.2 Chemicals

6.2.1 Sodium Sulfate - used for removing water from organic solvents before concentration step. Prepare by thoroughly rinsing with hexane and drying at 110°C overnight before use.

7. Procedure

7.1 Cleaning Glassware. All glassware shall be cleaned by the following procedure as described in Section 3A of the 1980 issue of "Manual of Analytical Methods for Analysis of Pesticide Residues in Human and Environmental Samples". See Appendix 2 for details.

1. Removal of surface residuals immediately after use.
2. Hot soak to loosen and flotate most of residue.

3. Hot water rinse to flush away flotated residue.
4. Soak with deep penetrant or oxidizing agent to destroy traces of organic material.
5. Hot water rinse to flush away materials loosened by deep penetrant soak.
6. Distilled water rinse to remove metallic deposits from the tap water.
7. Acetone rinse to flush off any final traces of organic material.
8. A preliminary flush of the glassware just before using with the same solvent to be used in the analysis.

7.2 Sample Preparation

7.2.1 Container No. 1 (Contents of 1st three impingers) - Note the physical properties of the sample as to color, consistency, presence of solids, and measure the volume and the pH. Spike the sample as necessary with TCDD and TCDF for QC purposes (see Appendix 2) and add the internal standard, tribromobiphenyl. Bring to known volume with water, mix well and remove 10 mL for Cl^- analysis by ion chromatography. Without adjusting the sample pH, transfer the impinger solutions to a 1000 mL separatory funnel. Rinse the sample container with 20 mL of acetone, followed by two 20 mL portions of hexane, adding the rinses to the separatory funnel. Extract the sample with 3 separate 100 mL aliquots of hexane. Split the resulting extract into two equal portions, transferring one-half to a Kuderna-Danish (K-D) evaporator. The other half is transferred to a hexane rinsed amber glass container, and is utilized for additional analyses for TCDD and TCDF. The portion transferred to the K-D is first filtered through pre-extracted, dried Na_2SO_4. The volume is reduced to the necessary level and then brought up to a known volume. Analyze the sample by the methods discussed in Section 7.3.

7.2.2 Container No. 2 (Hexane, acetone rinse of probe, Teflon line, impingers, and any miscellaneous glassware) - Note the physical properties of the sample as to color, consistency, presence of solids, and measure the volume. Spike the original solvent sample as necessary with the required compounds TCDD and TCDF for QC purposes and add the internal standard, tribromobiphenyl. Make the sample up to a known volume by adding the required amount of solvent. Split the sample into two equal portions, transferring one-half to a K-D evaporator. The other half is transferred to a hexane rinsed amber glass container, and is utilized for additional analyses for TCDD and TCDF. A 10 mL aliquot is removed from the portion transferred to the K-D and extracted with a known amount of water (10 mL) which is then analyzed for Cl^- by ion chromatography. (If the sample is present in more than one phase, split each phase into two equal portions.) Proceed with the concentration step as described in Section 7.2.1. Analyze the sample by the methods discussed in Section 7.3.

7.2.3 Container No. 3 (Contents of 4th and 5th impingers and water rinses) -Note the physical properties of the sample as to color, consistency, presence of solids, and measure the volume and the pH. Spike the samples with TCDD and TCDF for QC purposes, and add the internal standard, tribromobiphenyl. Make the sample up to a known volume by adding the required amount of water, mix well and remove 10 mL for Cl^- analysis by ion chromatography. Hold this sample in reserve for analysis, if required, at a later date. If sample preparation and analysis are required, proceed as outlined in Section 7.2.1. Store the sample in the dark at sub-ambient temperatures.

7.2.4 Florisil and XAD-2 Adsorbent - Observe and note the physical properties of the sample. Spike the sample with TCDD and TCDF directly into the adsorbents before being removed from the glass sorbent trap. Expel the entire contents of the sorbent trap into a glass extraction thimble with a course-fritted bottom. The Florisil and XAD-2 are extracted separately.

Cover the resin in the thimble with glass wool (or an equivalent device) to prevent the resin from floating out into the Soxhlet. If the resin is "wet" from the condensation of water, the resin should be packed loosely in the thimble to allow it to float, but remain confined to the thimble.

Rinse the sorbent trap with 10 mL acetone and then three 10 mL portions hexane, and put these rinses into the receiver. Assemble the Soxhlet extractor after charging with 250 mL hexane. Extract for 20 hours with a cycle time of 10 to 14 times per hour.

Split the resulting extract into two equal portions, transferring one-half to a K-D evaporator. The other half is transferred to a hexane rinsed amber glass container, and is utilized for additional analyses for TCDD or TCDF. Proceed with the concentration step as described in Section 7.2.1. Analyze the sample by the methods discussed in Section 7.3.

7.2.5 Raw Waste - Note the physical properties of the raw waste. Split the sample into two equal portions. One half is held in reserve or utilized for additional analyses as required. A known volume of the other half is appropriately diluted with hexane to bring the concentration of PCBs into the working range of the standards used for the analyses. A portion of the diluted raw waste can be subjected to a cleanup procedure, if necessary, before analysis by GC/MS. This cleanup can be performed utilzing Florisil column chromatography to remove polar compounds (Reference 2).

7.2.6 Sample Analysis Priorities - A total of six test run samples will be analyzed. The first set of three will be analyzed in the following order after sample preparation.

A. Combine the hexane extracts of the impinger (Container No. 1) and the acetone and hexane rinses of the probe etc. (Container No. 2) into one sample for analysis.
B. Florisil Extract
C. XAD-2 Extract

If the results of the XAD-2 extract analysis indicate that no PCB's are present then;

1) the basic impinger solutions will not be extracted,
2) no further XAD-2 extracts will be analyzed, and
3) A and B above will be combined for the 2nd set of three test run samples.

An exception to this would be the case in which the PCB levels found in analysis of a combined sample from the second set of three was significantly higher than previously found.

7.3 Analysis

7.3.1 GC/ECD Analysis - This method uses a temperature programmable GC equipped with an electron capture detector and fitted with a capillary column. Data will be acquire on a data system which has the capability of processing capillary peaks. Standards will be comprised of various Aroclors, as well as individual isomers.

7.3.1.1 Interferences. The specificity of the detector and the high resolution of the capillary column minimize the potential interferences.

7.3.1.2 Sample Extraction. Sample extractions will be performed using distilled-in-glass hexane (Burdick and Jackson) or equivalent. Samples will be concentrated to 1.0 mL using a K-D evaporator. Additional concentration down to 0.1 mL may be performed if necessary.

7.3.1.3 Sample Cleanup. It may be possible to analyze the extracted samples directly or diluted without further cleanup. The analysis itself will be the criteria for determining the need for further cleanup. If cleanup is required, use the Florisil method as described in Reference 2.

7.3.1.4 GC Conditions. A fused silica glass capillary column, SE-54, 30 meter x .25 mm I.D. will be used to achieve the necessary compound resolution. The temperature program used will give the best possible resolution of compounds. The program is 100°C to 270°C at 3°/min., holding at 270 until all peaks elute. The injector and detector temperatures will be greater than the highest temperature achieved in the temperature program and will be set at 300 and 250°C respectively. A 1-5 µL sample size injection is made dependent on the sample concentration. Pure nitrogen or other suitable carrier gas will be used. The use of an oxygen scavenger on the carrier is standard procedure. Similar columns will be used for the GC/ECD analyses and for the GC/MS analyses.

7.3.1.5 Qualitative Identification of PCBs. Selected samples and diluted raw waste will be initially screened by GC/ECD and GC/MS to determine the number and intensity of potential PCB peaks. Selected Aroclor mixes and individual PCB isomer standards will be prepared and analyzed by GC/ECD to tentatively identify the observed peaks by retention time. Confirmation by GC/MS using a similar column will be performed.

7.3.1.6 Quantitative Measurement of PCB Isomers. Once the individual isomers have been confirmed, a calibration curve and response factors will be developed. If necessary, the sample will be diluted to bring the concentration level into the range of the standards. The concentration of a particular isomer will be determined by comparing the area counts of the unknown to those of the standard.

7.3.1.7 Detection Limit. The minimum detectable limit is 50 pg per μL injected sample.

7.3.2 GC/MS Analysis - The method is designed primarily to address the problem of measurement of PCB emissions from combustion sources.

The method uses an automated gas chromatograph/mass spectrometer. Data are acquired in a select subset of masses and integrated according to gas chromatographic retention time criteria. Data are reported as quantity of monochloro-, dichloro-.........decachlorobiphenyl.

7.3.2.1 Interferences. Interferences in the PCB analysis are minimized with this procedure. Isotope abundance patterns are used to verify the composition as a PCB. Selected mass chromatograms and retention time windows provide a high degree of specificity in the analysis of a specie as a PCB.

7.3.2.2 Sample Extraction. Sample extractions will be done using distilled-in-glass hexane (Burdick and Jackson). Samples will be concentrated to 1.0 mL using a Kuderna-Danish evaporator. If necessary to achieve a minimum detectable quantity, samples will be further reduced in volume.

7.3.2.3 Sample Cleanup. It may be possible to analyze the extracted samples directly without further cleanup. The analysis itself will be the criteria for determining the need for further cleanup as described for the Standard EPA method for PCBs in industrial effluents (Reference 2). If cleanup is required, use the Florisil/silica gel procedures described in the EPA method.

7.3.2.4 GC Conditions. A 30 meter x 0.25 mm I.D. fused silica, SE-54, capillary column will be used. A temperature program at 3°C per minute from 100°C to 270°C (hold for 20 minutes) has been demonstrated to produce adequate separation and repeatability from run to run. A 1-5 μL sample size injection is made dependent on the concentration in the sample. The GC gas stream is diverted initially, allowing the solvent (hexane) to elute and be vented, and then the diverter is closed and data acquisition initiated.

7.3.2.5 GC/LRMS Conditions. Exact conditions will depend on spectrometer type and condition. Care should be taken to calibrate the mass scale to accommodate the significant mass defect of the PCBs. It is recommended that an Aroclor mixture will be used to construct an alternate mass calibration scale for the PCB analysis. The mass ranges for data acquisition will be set as follows:

PCB Group	Range	Analytical m/e
Cl_1	186 - 190	188
Cl_2	200 - 226	224
Cl_3	254 - 260	258
Cl_4	288 - 294	292
Cl_5	322 - 328	326
Cl_6	356 - 364	362
Cl_7	392 - 400	394
Cl_8	426 - 434	428
Cl_9	460 - 468	464
Cl_{10}	494 - 504	498

Integration times may vary slightly. A setting of 50-64 msec/amu will be used.

7.3.2.6 GC/HRMS Conditions. Analysis of waste and emission samples will be carried out using the basic methods of Tindall, et. al. (Reference 3) with certain modifications. Because of the expected complex nature of the waste samples, gas chromatographic separations will be effected with high efficiency fused silica capillary columns. Mass spectral observation, confirmation, and quantitation of PCBs (and other materials if desired) will employ a sequence of limited mass range scans encompassing the principle ions of interest. If the nature of the sample warrants, the mass spectral data can be acquired at resolving powers of 2500 or higher, reducing the incidence of interferences and potential false positives. Regions of the chromatograms designated for specific PCB observation will be defined both with modified Kovat's indices, as well as specific PCB isomers. Quantitation will be accomplished against a spiked internal standard using relative response factors measured against individual PCB isomers.

7.3.2.7 Qualitative Identification of PCBs. A total ion chromatogram will be constructed from the sum of all the mass used in data acquisition. Individual mass spectra will be obtained at GC peak maxima. These spectra will be examined to determine whether the proper isotope abundance patterns are present for the given chlorobiphenyl group.

7.3.2.8 Quantitative Measurement of PCB Groups. When the species have been confirmed as PCBs, individual mass chromatograms will be obtained for the analytical masses corresponding to the PCB groups, 188, 224, --- 498. An Aroclor sample such as Aroclor 1232 and Aroclor 1254 will be used to establish a relative retention time (RRT) scale using the data given by Webb and McCall (Reference 4). The area for each PCB group is integrated over the RRT regions indicated below:

PCB Group	Analytical m/e	RRT Region
Cl_1	188	0(5) - 20
Cl_2	224	15 - 35
Cl_3	258	25 - 55
Cl_4	292	40 - 100
Cl_5	326	70 - 150
Cl_6	363	125 - 250
Cl_7	394	160 - 350
Cl_8	428	275 - 600
Cl_9	464	400 -1000
Cl_{10}	498	650 -1200

The RRT windows may need to be adjusted slightly for proper measurement of total areas. Use of these windows minimizes interferences from other PCBs isomer groups.

7.3.2.9 Detection Limit. The detection limit of this method is expected to be in the range of 20 to 200 ng/µL injected (Reference 3).

7.3.3.0 Ion Chromatography (Cl^-) Analysis. Ion chromatography is the method of analysis to determine chloride (Cl^-) ion in all specified samples.

7.3.3.1 Analytical Conditions:

Chromatograph: Ion chromatograph, Dionex or equivalent
Column: 250 mm anion separator column and an anion suppressor
Eluent: 0.003 M $NaHCO_3$/0.0024 M Na_2CO_3 aqueous solution
Detector: Electrical Conductivity Detector
Regenerant: 1 N aqueous H_2SO_4 solution

7.3.3.2 Analysis. For anion analysis, the eluent (0.003 M $NaHCO_3$/0.0024 M Na_2CO_3) and separator column (containing anion resin in the HCO_3^-/CO_3^{2-} form) cause the sample ions to split into distinct bands. The retention time of each anion is influenced by the affinity of that ion, the eluent used, column length, and the eluent flow rate. The effluent from the separator column is then fed to the suppressor column. Two reactions occur in the suppressor column. The resin (a strong acid resin/H^+ form) removes Na^+ and protonates the HCO_3^-/CO_3^{2-} to H_2CO_3. Then, all the sample anions exit the suppressor column as the acid since the sample cations are exchanged for H^+ in the suppressor.

Quantitative results are calculated using a linear regression line obtained from a set of calibration standards. An example calculation is given below.

Standard Solution No.	Concentration	Peak Height
1	C_{s1}	P_{s1}
2	C_{s2}	P_{s2}
3	C_{s3}	P_{s3}

A linear regression analysis of these data yields the standard calibration equation

$$P_{s,i} = (\text{Line Slope}) \times (C_{s,i}) + (\text{Intercept}).$$

The peak height for an unknown, P_u, is measured as well as that of a blank, P_b. Concentrations $C_{u,\text{ measured}}$ and C_b are calculated using the standard calibration equation and $C_{u,\text{ corrected}}$ is calculated as

$$C_{u,\text{ corrected}} = C_{u,\text{ measured}} - C_b.$$

Due to the particular anions of interest, i.e., Cl^-, and their concentration levels, all samples will be diluted for quantitation with distilled deionized water.

Interferences resulting from co-eluting ions will be checked by method of addition using a standard chloride solution.

7.4 Quality Assurance/Quality Control

7.4.1 QC - All glassware will be cleaned before each sample by cleaning by the prescribed method given in Section 7.1. Soxhlet extractors will then be charged with hexane, assembled, and extracted for two hours. The hexane is concentrated in a K-D and analyzed for PCBs. A portion of this glassware "blank" extraction will be held in reserve or analyzed for additional compounds such as TCDD and TCDF as required.

All samples will be spiked before extraction with the appropriate internal standard.

Every sixth sample will be a QC sample containing an internal standard. A hexane "blank" will be run every seventh sample. An additional "blank" will be run following any highly concentrated samples to demonstrate the absence of "memory effects" for subsequent analyses.

Duplicate sample analyses will be performed once daily, or at a minimum of once every 10 samples.

7.4.2 QA - QA samples will be submitted for analysis from an external, independant source.

8. Analysis of On-Board Air Samples

Ambient air samples collected on board using NIOSH approved XAD-2 tubes will be extracted with 1 mL of hexane for 30 minutes and analyzed by GC/ECD for PCB's.

REFERENCES

1. Methods for Determining the Polychlorinated Biphenyl Emissions from Incineration and Capacitor and Transformer Filling Plants, EPA-600/4-77-048, November 1977.

2. Method for Polychlorinated Biphenyls (PCB's) in Industrial Effluents Federal Register 38, No. 75, Pt. II (1973).

3. Tindell, Willia G. and Percy E. Wininger, Journal of Chromatography, 196 (1980) 109-119.

4. Webb, R. G. and Ann C. McCall, J. Assoc. Offic. Anal. Chemists, 55, 746 (1972).

APPENDIX I (A,a)

Details of the glassware cleaning procedure discussed in Section 7.1.

1. As soon as possible after use of glassware coming in contact with PCB's, i.e., beakers, pipets, flasks or bottles used for standards, the glassware should be acetone flushed before placing in the hot detergent soak. If this is not done, the soak bath may serve to contaminate all other glassware placed therein. Many instances of widespread laboratory contamination are traceable to the glassware washing sink.

2. The hot soak consists of a bath of a suitable detergent in water of 50°C or higher. The detergent, powder or liquid, should be entirely synthetic and not a fatty acid base. There are very few areas of the country where the water hardness is sufficiently low to avoid the formation of some hard water scum resulting from the reaction between calcium and magnesium salts with a fatty acid soap. This hard water scum or curd would have an affinity particularly for the chlorinated compounds and, being almost wholly water insoluble, would deposit on all glassware in the bath in a thin film.

   There are many suitable detergents on the wholesale and retail market. Most of the common liquid dishwashing detergents sold at retail are satisfactory but are more expensive than other comparable products sold industrially. Alconox, in powder or tablet form is manufactured by Alconox, Inc., New York and is marketed by a number of laboratory supply firms. Sparkleen, another powdered product, is distributed by Fisher Scientific Company.

NOTE: Certain detergents, even in trace quantities, may contain organics that will contribute significant background contamination by electron capture detection. For this reason any detergent selected should be carefully checked to ensure freedom from such contamination. The following procedure is recommended:

Add 25 mL dist. water, previously checked for background contaminants, to a 250 mL sep funnel. Add 1 drop of the liquid detergent (50 mg if in powder form), followed by 100 mL hexane. Stopper funnel and shake vigorously for 2 minutes. Allow layer separation, draw off and discard aqueous layer. Add a pinch of anhydrous Na_2SO_4 to the hexane extract and shake 1 minute. Transfer extract to a Kuderna-Danish assembly fitted with a 10 mL evaporative concentrator tube containing one 3 mm glass bead. Reduce extract volume to ca 3 mL in a hot water bath. Cool, rinse down Ŧ joint and sides of tube with hexane, diluting extract to exactly 5 mL. Stopper tube and shake on Vortex mixer 1 minute. Chromatograph by electron capture GLC and evaluate chromatogram for contaminant peaks.

3. No comments required.

4. The most common and highly effective oxidizing agent for removal of traces of organic compounds is the traditional chromic acid solution made up of H_2SO_4 and potassium or sodium dichromate. For maximum efficiency, the soak solution should be hot (40° to 50°C). Safety precautions must be rigidly observed in the handling of this solution. Prescribed safety gear should include safety goggles, rubber gloves and apron. The bench area where this operation is conducted should be covered with lead sheeting as spattering will disintegrate the unprotected bench surface.

The potential hazards of using chromic sulfuric acid mixture are great and have been well publicized. There are now commerically available substitutes that possess the advantage of safety in handling. These are biodegradable concentrates with a claimed cleaning strength equal to the chromic acid solution. They are alkaline, equivalent to ca 0.1 N NaOH upon dilution and are claimed to remove dried blood, silicone greases, distillation residues, insoluble organic residues, etc. They are further claimed to remove radioactive traces and will not attach glass nor exert a corrosive effect on skin or clothing. One such product is "Chem Solv 2157," manufactured by Mallinckrodt and available through laboratory supply firms. Another comparable product is "Detex" a product of Borer-Chemie, Solothurn, Switzerland.

5, 6, and 7. No comments required.

8. There is always a possibility that between the time of washing and the next use, the glassware may pick up some contamination from either the air or direct contact. To ensure against this, it is good practice to flush the item immediately before use with some of the same solvent that will be used in the analysis.

This drying and storage of the cleaned glassware is of critical importance to prevent the beneficial effects of the scrupulous cleaning from being nullified. Pegboard drying is not recommended as contaminants may be introduced to the interior of the cleaned vessels. Neoprene-coated metal racks are suitable for such items as beakers, flasks, chromatographic tubes, and any glassware then can be inverted and suspended to dry. Small articles like stirring rods, glass stoppers and bottle caps can be wrapped in aluminum foil and oven dried a short time if oven space is available. Under no circumstance should such small items be left in the open without protective covering. The dust cloud raised by the daily sweeping of the laboratory floor can most effectively recontaminate the clean glassware.

PART B. ANALYSIS OF SAMPLES FOR THE DETERMINATION OF PCB EMISSIONS FROM SHIPBOARD LIQUID INCINERATORS

1. Principle and Applicability

1.1 Principle. Gaseous and particulate Polychlorinated Biphenyls (PCBs) are withdrawn from the source using a sampling train. The PCBs are collected in the Florisil adsorbent tube and in the impingers in front of the adsorbent. The Florisil is followed by an XAD-2 trap and two basic impingers. The total PCBs in the train are determined by solvent extraction followed by Gas Chromatography/Electron Capture Detection (GC/ECD) and/or Gas Chromatography/Mass Spectroscopy (GC/MS).

1.2 Applicability. This method is applicable to the determination of vaporous emissions from "shipboard liquid incinerators". The analysis of the samples should be conducted by chemical personnel experienced in determinations of trace organics utilizing sophisticated, instrumental techniques. All extract transfers should be made quantitatively by rinsing the apparatus at least three times with the appropriate solvent and adding the rinses to the receiving container. A pre-extracted boiling stone should be used in all evaporative steps to control "bumping".

2. Range and Minimum Detectable Limit (MDL)

The range of the analytical method may be expanded considerably through concentration and/or dilution. The total method sensitivity is also highly dependent on the volume of gases sampled. The MDL of the GC/ECD method is about 50 pg of total PCBs per 1 uL injection. The MDL of the GC/MS system ranges between 50-200 pg/uL.

3. Interferences

Organochlorine compounds other than PCB, Tetrachlorodibenzofuran (TCDF) or Tetrachlorodibenzodioxin (TCDD) found in the raw waste may interfere with the analyses. Appropriate sample cleanup steps shall be performed as needed.

Throughout all stages of sample handling and analysis, care should be taken to avoid contact of samples and extracts with synthetic organic materials other than TFE® (polytetrafluorethylene). Adhesives should not be used to hold TFE® liners on lids, (but, if necessary, appropriate blanks must be run).

4. Precision and Accuracy

From sampling with identical and paired sampling trains, the precision of the method has been determined to be 10 to 15% of the PCB concentration measured. Recovery efficiencies on source samples spiked with PCB compounds ranged from 85 to 95% (Reference 1).

5. Apparatus

5.1 Gas Chromatograph. The gas chromatograph (GC) will be equipped with an electron capture detector (ECD) for the detection and quantitation of PCBs. The GC should also be equipped with a capillary column (such as a fused silica SE-54, 30 meter x 0.25 mm) capable of resolving the PCB isomers utilizing the appropriate temperature programming.* The GC/ECD should be vented to a scrubber or vent for safety reasons. A compatible integrator should be used which has the ability to accurately integrate capillary peaks.

5.2 Gas Chromatograph/Mass Spectrometer/Data System. The gas chromatograph/mass spectrometer (GC/MS) should be equipped with a capillary column capable of resolving the PCB isomers. The MS system will have the capability of both total ion monitoring, as well as selective ion monitoring up to mass number 500.

5.3 Glassware

5.3.1 Soxhlet extractors - used for the extraction of the XAD-2 and Florisil adsorbents. Select the proper size Soxhlet to accomodate the volume of adsorbent.

5.3.2 Kuderna-Danish Evaporator - used to reduce the volume of solvent.

5.3.3 Separatory funnel - equipped with a Teflon stop-cock used for extraction of impinger solutions.

5.3.4 Miscellaneous volumetric glassware - used for determining the volume of solvent.

5.4 pH Meter. A pH meter equipped with appropriate glass and reference electrodes for measuring the pH of the collected samples.

---

*The use of capillary columns is referenced in this document for the separation of PCB isomers. Other columns may be used if they can be demonstrated to be adequate for the specific task.

5.5 Glass Wool. Cleaned by thorough rinsing with hexane, dried in an oven at 110°C, and stored in a hexane-washed glass jar with TFE-lined screw caps.

6. Reagents and Chemicals

6.1 Solvents. Pesticide quality, Burdick and Jackson "Distilled in Glass" or equivalent, stored in original containers. A blank must be screened by the analytical detection method.

6.1.1 Acetone

6.1.2 Hexane

6.2 Chemicals

6.2.1 Sodium Sulfate - used for removing water from organic solvents before concentration step. Prepare by thoroughly rinsing with hexane and drying at 110°C overnight before use.

7. Procedure

7.1 Cleaning Glassware. All glassware shall be cleaned by the following procedure as described in Section 3A of the 1980 issue of "Manual of Analytical Methods for Analysis of Pesticide Residues in Human and Environmental Samples". See Appendix I for details.

1. Removal of surface residuals immediately after use.
2. Hot soak to loosen and flotate most of residue.
3. Hot water rinse to flush away flotated residue.
4. Soak with deep penetrant or oxidizing agent to destroy traces of organic material.
5. Hot water rinse to flush away materials loosened by deep penetrant soak.
6. Distilled water rinse to remove metallic deposits from the tap water.
7. Acetone rinse to flush off any final traces of organic material.
8. A preliminary flush of the glassware just before using with the same solvent to be used in the analysis.

7.2 Sample Preparation

7.2.1 Container No. 1 (Contents of 1st three impingers) - Note the physical properties of the sample as to color, consistency, presence of solids, and measure the volume and the pH. Spike the sample as necessary with the required compounds (such as TCDD and TCDF) for QC purposes and add an internal standard (such as tribromobiphenyl). Without adjusting the sample pH, transfer the impinger solutions to a 1000 mL separatory funnel. Rinse the sample container with 20 mL of acetone, followed by two 20 mL portions of hexane, adding the rinses to the separatory funnel. Extract the sample with 3 separate 100 mL aliquots of hexane. Split the resulting extract into two equal portions, transferring one-half to a Kuderna-Danish (K-D) evaporator. The other half is transferred to a hexane rinsed amber glass container, and is held in reserve or utilized for additional analyses as specified for such compounds as TCDD or TCDF, as required. The portion transferred to the K-D is first filtered through pre-extracted, dried Na_2SO_4. The volume is reduced to the necessary level and then brought up to a known volume. Analyze the sample by the methods discussed in Section 7.3.

7.2.2 Container No. 2 (Hexane, acetone rinse of probe, Teflon line, impingers, and any miscellaneous glassware) - Note the physical properties of the sample as to color, consistency, presence of solids, and measure the volume. Spike the original solvent sample as necessary with the required compounds (such as TCDD and TCDF) for QC purposes and add an internal standard (such as tribromobiphenyl). Make the sample up to a known volume by adding the required amount of solvent. Split the sample into two equal portions, transferring one-half to a K-D evaporator. The other half is transferred to a hexane rinsed amber glass container, and is held in reserve or utilized for additional analyses for specified compounds such as TCDD or TCDF, as required. (If the sample is present in more than one phase, split each phase into two equal portions.) Proceed with the concentration step as described in Section 7.2.1. Analyze the sample by the methods discussed in Section 7.3.

7.2.3 Container No. 3 (Contents of 4th and 5th impingers and water rinses) Note the physical properties of the sample as to color, consistency, presence of solids, and measure the volume and the pH. Spike the samples as necessary with the required compounds (such as TCDD and TCDF) for QC purposes, and add an internal standard (such as tribromobiphenyl). Make the sample up to a known volume by adding the required amount of solvent. Hold this sample in reserve for analysis, if required, at a later date. If sample preparation and analysis are required, proceed as outlined in Section 7.2.1. Store the sample in the dark at sub-ambient temperatures.

7.2.4 Florisil and XAD-2 Adsorbent - Observe and note the physical properties of the sample. Spike the sample as necessary with the required compounds (such as TCDD and TCDF) directly into the adsorbents before being removed from the glass sorbent trap. Expel the entire contents of the sorbent trap into a glass extraction thimble with a course-fritted bottom. The Florisil and XAD-2 are extracted separately.

Cover the resin in the thimble with glass wool (or an equivalent device) to prevent the resin from floating out into the Soxhlet. If the resin is "wet" from the condensation of water, the resin should be packed loosely in the thimble to allow it to float, but remain confined to the thimble.

Rinse the sorbent trap with 10 mL acetone and then three 10 mL portions hexane, and put these rinses into the receiver. Assemble the Soxhlet extractor after charging with 250 mL hexane. Extract for 20 hours with a cycle time of 10 to 14 times per hour.

Split the resulting extract into two equal portions, transferring one-half to a K-D evaporator. The other half is transferred to a hexane rinsed amber glass container, and is held in reserve or utilized for additional analyses as specified for such compounds as TCDD or TCDF as required. Proceed with the concentration step as described in Section 7.2.1. Analyze the sample by the methods discussed in Section 7.3.

7.2.5 Raw Waste - Note the physical properties of the raw waste. Split the sample into two equal portions. One half is held in reserve or utilized for additional analyses as required. A known volume of the other half is appropriately diluted with hexane to bring the concentration of PCBs into the working range of the standards used for the analyses. A portion of the diluted raw waste can be subjected to a cleanup procedure, if necessary, before analysis by GC/MS. This cleanup can be performed utilzing Florisil column chromatography to remove polar compounds (Reference 2).

7.2.6 Sample Analysis Priorities - Samples may be analyzed individually or combined into a single sample depending upon the overall information desired and the levels of PCBs expected.

7.3 Analysis

7.3.1 GC/ECD Analysis - This method uses a temperature programmable GC equipped with a suitable detector such as an electron capture or Hall®, and fitted with a capillary column. Data are acquired on a data system which has the capability of processing capillary peaks. Standards will be comprised of various Aroclors, as well as individual isomers.

7.3.1.1 Interferences. The specificity of the detector and the high resolution of the capillary column minimize the potential interferences.

7.3.1.2 Sample Extraction. Sample extractions should be performed using distilled-in-glass hexane (Burdick and Jackson) or equivalent. Samples should be concentrated to 1.0 mL using a K-D evaporator. Additional concentration down to 0.1 mL may be performed if necessary.

7.3.1.3 Sample Cleanup. It may be possible to analyze the extracted samples directly or diluted without further cleanup. The analysis itself should be the criteria for determihing the need for further cleanup. If cleanup is required, use the Florisil method as described in Reference 2.

7.3.1.4 GC Conditions. Use a glass capillary column such as a fused silica (SE-54, 30 meter x .25 mm I.D.) to achieve the necessary compound resolution. The temperature program selected should be one that gives the best possible resolution of compounds (for example, $100^{\circ}C$ to $270^{\circ}C$ at 3°/min., holding at 270 until all peaks elute). The injector and detector temperatures should be greater than the highest temperature achieved in the temperature program. A 1-5 µL sample size injection is made dependent on the sample concentration. Pure nitrogen or other suitable carrier gas should be used. The use of an oxygen scavenger on the carrier is recommended. It is recommended that similar columns be used for the GC/ECD analyses as used for the GC/MS analyzers.

7.3.1.5 Qualitative Identification of PCBs. Selected samples and diluted raw waste will be initially screened by GC/ECD to determine the number and intensity of potential PCB peaks. Selected Aroclor mixes and individual PCB isomer standards will be prepared and analyzed by GC/ECD to tentatively identify the observed peaks by retention time. Confirmation by GC/MS using a similar column will be performed.

7.3.1.6 Quantitative Measurement of PCB Isomers. Once the individual isomers have been confirmed, a calibration curve and response factors will be developed. If necessary, the sample will be diluted to bring the concentration level into the range of the standards. The concentration of a particular isomer will be determined by comparing the area counts of the unknown to those of the standard.

7.3.1.7 Detection Limit. The minimum detectable limit is 50 pg per µL injected sample.

7.3.2 GC/MS Analysis - The method is designed primarily to address the problem of measurement of PCB emissions from combustion sources.

The method uses an automated gas chromatograph/mass spectrometer. Data are acquired in a select subset of masses and integrated according to gas chromatographic retention time criteria. Data are reported as quantity of monochloro-, dichloro-.........decachlorobiphenyl.

7.3.2.1 Interferences. Interferences in the PCB analysis are minimized with this procedure. Isotope abundance patterns are used to verify the composition as a PCB. Selected mass chromatograms and retention time windows provide a high degree of specificity in the analysis of a specie as a PCB.

7.3.2.2 Sample Extraction. Sample extractions should be done using distilled-in-glass hexane (Burdick and Jackson). Samples should be concentrated to 1.0 mL using a Kuderna-Danish evaporator. If necessary to achieve a minimum detectable quantity, samples may be further reduced in volume.

7.3.2.3 Sample Cleanup. It may be possible to analyze the extracted samples directly without further cleanup. The analysis itself should be the criteria for determining the need for further cleanup as described for the Standard EPA method for PCBs in industrial effluents (Reference 2). If cleanup is required, use the Florisil/silica gel procedures described in the EPA method.

7.3.2.4 GC Conditions. Use a 30 meter x 0.25 mm I.D. fused silica capillary column containing any of several phases. Appropriate phases such as SE-54 and DB-5 (0.25 micron film) are acceptable and have been used successfully for PCB analysis. A temperature program at $3^{o}C$ per minute from 100°C to 270°C (hold for 20 minutes) has been demonstrated to produce adequate separation and repeatability from run to run. A 1-5 µL sample size injection is made dependent on the concentration in the sample. The GC gas stream is diverted initially, allowing the solvent (hexane) to elute and be vented, and then the diverter is closed and data acquisition initiated.

7.3.2.5 GC/LRMS Conditions. Exact conditions will depend on spectrometer type and condition. Care should be taken to calibrate the mass scale to accommodate the significant mass defect of the PCBs. It is recommended that an Aroclor mixture will be used to construct an alternate mass calibration scale for the PCB analysis. Set the mass ranges for data acquisition as follows:

PCB Group	Range	Analytical m/e
Cl_1	186 - 190	188
Cl_2	200 - 226	224
Cl_3	254 - 260	258
Cl_4	288 - 294	292
Cl_5	322 - 328	326
Cl_6	356 - 364	362
Cl_7	392 - 400	394
Cl_8	426 - 434	428
Cl_9	460 - 468	464
Cl_{10}	494 - 504	498

Integration times will vary with instruments. A setting of 50-64 msec/amu is recommended.

7.3.2.6 GC/HRMS Conditions. Analysis of waste and emission samples will be carried out using the basic methods of Tindall, et. al. (Reference 3) with certain modifications. Because of the expected complex nature of the waste samples, gas chromatographic separations will be effected with high efficiency fused silica capillary columns. Mass spectral observation, confirmation, and quantitation of PCBs (and other materials if desired) will employ a sequence of limited mass range scans encompassing the principle ions of interest. If the nature of the sample warrants, the mass spectral data can be acquired at resolving powers of 2500 or higher, reducing the incidence of interferences and potential false positives. Regions of the chromatograms designated for specific PCB observation will be defined both with modified Kovat's indices, as well as specific PCB isomers. Quantitation will be accomplished against a spiked internal standard using relative response factors measured against individual PCB isomers.

7.3.2.7 Qualitative Identification of PCBs. A total ion chromatogram is constructed from the sum of all the mass used in data acquisition. Individual mass spectra are obtained at GC peak maxima. These spectra are examined to determine whether the proper isotope abundance patterns are present for the given chlorobiphenyl group.

7.3.2.8 Quantitative Measurement of PCB Groups. When the species have been confirmed as PCBs, individual mass chromatograms are obtained for the analytical masses corresponding to the PCB groups, 188, 224, --- 498. An Aroclor sample such as Aroclor 1232 and Aroclor 1254 is used to establish a relative retention time (RRT) scale using the data given by Webb and McCall (Reference 3). The area for each PCB group is integrated over the RRT regions indicated below:

PCB Group	Analytical m/e	RRT Region
Cl_1	188	0(5) - 20
Cl_2	224	15 - 35
Cl_3	258	25 - 55
Cl_4	292	40 - 100
Cl_5	326	70 - 150
Cl_6	363	125 - 250
Cl_7	394	160 - 350
Cl_8	428	275 - 600
Cl_9	464	400 -1000
Cl_{10}	498	650 -1200

The RRT windows may need to be adjusted slightly for proper measurement of total areas. Use of these windows minimizes interferences from other PCB groups.

7.3.2.9 Detection Limit. The detection limit of this method is expected to be in the range of 20 to 200 ng/µL injected (Reference 4).

7.4 Quality Assurance/Quality Control

7.4.1 QC - All glassware will be cleaned before each sample by cleaning by the prescribed method given in Section 7.1. Soxhlet extractors will then be charged with hexane, assembled, and extracted for two hours. The hexane is concentrated in a K-D and analyzed for PCBs. A portion of this glassware "blank" extraction will be held in reserve or analyzed for additional compounds such as TCDD and TCDF as required.

All samples will be spiked before extraction with the appropriate internal standard.

Every sixth sample will be a QC sample containing an internal standard. A hexane "blank" will be run every seventh sample. An additional "blank" will be run following any highly concentrated samples to demonstrate the absence of "memory effects" for subsequent analyses.

Duplicate sample analyses will be performed once daily, or at a minimum of once every 10 samples.

7.4.2 QA - QA samples will be submitted for analysis from an external, independent source.

REFERENCES

1) Methods for Determining the Polychlorinated Biphenyl Emissions from Incineration and Capacitator and Transformer Filling Plants, EPA-600/4-77-048, November 1977.

2) Method for Polychlorinated Biphenyls (PCBs) in Industrial Effluents, Federal Register 38, No. 75, Pt. II (1973).

3) Webb, R. G. and McCall, Ann C., J. Assoc. Offic. and Chemists, 55, 746 (1972).

4) Tindall, William G. and Wininger, Percy E., Journal of Chromatography, 196 (1980) 109-119.

APPENDIX I (A,b)

DETAILS OF THE GLASSWARE CLEANING PROCEDURE DISCUSSED IN SECTION 7.1

1. As soon as possible after use of glassware coming in contact with PCBs, i.e., beakers, pipets, flasks, or bottles used for standards, the glassware should be acetone flushed before placing in the hot detergent soak. If this is not done, the soak bath may serve to contaminate all other glassware placed therein. Many instances of widespread laboratory contamination are traceable to the glassware washing sink.

2. The hot soak consists of a bath of a suitable detergent in water of 50°C or higher. The detergent, powder or liquid, should be entirely synthetic and not a fatty acid base. There are very few areas of the country where the water hardness is sufficiently low to avoid the formation of some hard water scum resulting from the reaction between calcium and magnesium salts with a fatty acid soap. This hard water scum or curd would have an affinity particularly for the chlorinated compounds and, being almost wholly water insoluble, would deposit on all glassware in the bath in a thin film.

   There are many suitable detergents on the wholesale and retail market. Most of the common liquid dishwashing detergents sold at retail are satisfactory, but are more expensive than other comparable products sold industrially. Alconox, in powder or tablet form, is manufactured by Alconox, Inc., New York and is marketed by a number of laboratory supply firms. Sparkleen, another powdered product, is distributed by Fisher Scientific Company.

   NOTE: Certain detergents, even in trace quantities, may contain organics that will contribute significant background contamination by electron capture detection. For this reason, any detergent selected should be carefully checked to ensure freedom from such contamination. The following procedure is recommended:

   Add 25 mL dist. water, previously checked for background contaminants, to a 250 mL sep funnel. Add 1 drop of the liquid detergent (50 mg if in powder form), followed by 100 mL hexane. Stopper funnel and shake vigorously for 2 minutes. Allow layer separation, draw off and discard aqueous layer. Add a pinch of anhydrous Na_2SO_4 to the hexane extract and shake 1 minute. Transfer extract to a Kuderna-Danish assembly fitted with a 10 mL evaporative concentrator tube containing one 3 mm glass bead. Reduce extract volume to ca 3 mL in a hot water bath. Cool, rinse down Ŧ joint and sides of tube with hexane, diluting extract to exactly 5 mL. Stopper tube and shake on Vortex mixer 1 minute. Chromatograph by electron capture GLC and evaluate chromatogram for contaminant peaks.

3. No comments required.

4. The most common and highly effective oxidizing agent for removal of traces of organic compounds is the traditional chromic acid solution made up of H_2SO_4 and potassium or sodium dichromate. For maximum efficiency, the soak solution should be hot (40°C to 50°C). Safety precautions must be rigidly observed in the handling of this solution. Prescribed safety gear should include safety goggles, rubber gloves, and apron. The bench area where this operation is conducted should be covered with lead sheeting as spattering will disintegrate the unprotected bench surface.

   The potential hazards of using chromic sulfuric acid mixture are great and have been well publicized. There are now commercially available substitutes that possess the advantage of safety in handling. These are biodegradable concentrates with a claimed cleaning strength equal to the chromic acid solution. They are alkaline, equivalent to ca 0.1 N NaOH upon dilution and are claimed to remove dried blood, silicone greases, distillation residues, insoluble organic residues, etc. They are further claimed to remove radioactive traces and will not attach glass nor exert a corrosive effect on skin or clothing. One such product is "Chem Solv 2157," manufactured by Mallinckrodt and available through laboratory supply firms. Another comparable product is "Detex," a product of Borer-Chemie, Solothurn, Switzerland.

5, 6, and 7. No comments required.

8. There is always a possibility that between the time of washing and the next use, the glassware may pick up some contamination from either the air or direct contact. To ensure against this, it is good practice to flush the item immediately before use with some of the same solvent that will be used in the analysis.

The drying and storage of the cleaned glassware is of critical importance to prevent the beneficial effects of the scrupulous cleaning from being nullified. Pegboard drying is not recommended as contaminants may be introduced to the interior of the cleaned vessels. Neoprene-coated metal racks are suitable for such items as beakers, flasks, chromatographic tubes, and any glassware then can be inverted and suspended to dry. Small articles like stirring rods, glass stoppers and bottle caps can be wrapped in aluminum foil and oven dried a short time if oven space is available. Under no circumstance should such small items be left in the open without protective covering. The dust cloud raised by the daily sweeping of the laboratory floor can most effectively recontaminate the clean glassware.

APPENDIX I (B)

RTI COMMENTS ON ANALYSIS PROTOCOL

RESEARCH TRIANGLE INSTITUTE
POST OFFICE BOX 12194
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27709

SYSTEMS AND MEASUREMENTS DIVISION

September 20, 1982

Mr. Gary L. Johnson,
Quality Assurance Officer
Technical Support Staff
MD 62
Industrial Environmental Research Laboratory
U.S Environmental Protection Agency
Research Triangle Park, NC 27711

Dear Mr. Johnson:

RTI has reviewed the draft plans entitled "Draft Analysis Plan for the At-Sea Incineration of PCB-Wastes Onboard the M/T Vulcanus" and "Part B - Analysis of Samples for the Determination of PCB Emissions from Shipboard Liquid Incinerators" prepared by TRW under EPA Contract 68-02-3174, WA 103 for IERL/RTP. The IERL project officers are Merrill Jackson and Larry Johnson.

The review process consisted of evaluation of the reports for technical content and as an aid to preparation of the quality assurance plan as per the EPA QAMs-005/80 guidelines.

If you have further questions regarding our comments, please call me at 541-6738.

Sincerely,

D. E. Lentzen /ac

D. E. Lentzen, Ph.D.
Environmental Scientist

DEL/ac

cc: Judy Ford, EPA (4)
    Alvia Gaskill

File: 43U-1847-39

(919) 541-6000 FROM RALEIGH, DURHAM AND CHAPEL HILL

REVIEW OF TRW ANALYSIS PLANS FOR AT-SEA INCINERATION OF PCB-WASTES

by

Alvia Gaskill, Jr.
Donald E. Lentzen
Arthur Mosely
Edo Pellizzari

EPA Contract No. 68-02-3146
Task 151

RTI Project 1847-51

EPA Project Officer
Gary L. Johnson

Prepared for

TECHNICAL SUPPORT STAFF
INDUSTRIAL ENVIRONMENTAL RESEARCH LABORATORY
ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27711

September 1982

TECHNICAL REVIEW OF THE ANALYSIS PLAN FOR THE AT-SEA INCINERATION OF PCB WASTE ON BOARD THE M/T VULCANUS

N.B. Comments included herein relate only to the PCB analysis procedures proposed. Dioxin and furan analyses will be reviewed by another organization.

Reference to both draft plans will be made in the following comments. The September 1982 draft entitled "Analysis Plan for At-Sea...Onboard the M/T Vulcanus" will be referred to as Draft 1, and the draft entitled "Part B..." will be referred to as Draft 2 throughout these comments. Comments are listed consecutively according to the section numbers which are consistent for both Draft 1 and 2.

Section 1 Principle and Applicability

- There is a footnote at the bottom of page 1 of Draft 1 with words missing.

Section 2 Range and Minimum Detectable Limit (MDL)

- In Section 2 of both drafts, an MDL of 50-200 pg/ L is given for the GC/MS system to be used, whereas in Section 7.3.2.9, the detection limit given is 20-200 ng/ L. The latter value is a more reasonable MDL. Which one is the goal for this study?

Section 3 Interferences

- The authors note that "if necessary, appropriate blanks must be run." Due to the sensitivity of an electron capture detector (ECD), blanks should be run on each step of the procedure. Batches of cleaned glassware, such as vials, pipets, etc., should be screened as blanks to ensure a low background of PCBS. Blanks of the glass wool (Section 5.6), sodium sulfate (Section 6.2.1) TFE cylinders and evaporation "chips" should also be obtained.

Section 4 Precision and Accuracy

- In both drafts, historical experience of 85-95% recoveries of PCB spiked samples is given. What are the precision and accuracy acceptance criteria for the vulcanus samples? Are they the same?

Section 5 Apparatus

- There is a footnote at the bottom of page 2 of Draft 2 that doesn't appear in Draft 1.
- Draft 1 lists an ion chromatograph. Draft 2 does not. Will IC analyses for Cl^- be performed?

Section 6 Reagents and Chemicals

- As noted, blanks of the pesticide quality solvents must be screened by the analytical detection method. It is important that any solvent which will be concentrated via Kuderna-Danish evaporators be concentrated further than the anticipated concentration factor. This concentrate must be screened by the analytical detection method. Different lots of solvents should be screened, and when an adequate lot is identified, this lot should be stockpiled for future use. Screening of different lots, and the use of the cleanest lot is preferred to trying to clean up dirty lots via redistillation.

Section 7.1 Cleaning Glassware

- There is no Appendix 2 in either draft. Appendix 1 is the source of glassware cleaning details.
- An additional cleaning step consisting of a high temperature backout (475° C for 2 hours) may be necessary. This step may be substituted for the chromic acid wash for items such as vials and pipets, particularly for "first use" of these items. If possible, new glassware should be procured and dedicated for PCB analyses.

Section 7.2 Sample Preparation

- The discussion given in the two drafts differs markedly. For example, Draft 1 calls for preparation for IC analyses. Draft 2 does not.
- Draft 1 says that TBB will be the internal standard. Draft 2 says it could be. This creates confusion and should be resolved before analyses are conducted.
  We also disagree with the use of TBB as an "internal standard." By adding it to the sample prior to extraction it is really a surrogate standard since it will have to experience some degree of extraction efficiency. Internal standards are generally added to a sample just prior to analysis to monitor analytical accuracy and precision.

Section 7.2.1 Sample Preparation

- Tribromobiphenyl (TBB) is specified for use as the "internal standard." TBB is probably a suitable "internal standard," the use of more than one internal standard is preferred. Studies in our laboratory have shown that best results are obtained when several internal standards are used, such that the standards cover the volatility range of the target compounds. There are several advantages to the use of multiple internal standards. First, if an interference peak obscures one of the internal standards, another internal standard can be used for quantitation. Secondly, multiple internal standards covering the volatility range of the target compounds correct for any sample discrimination occurring during the injection of the sample onto the GC column. Sample discrimination, where more of the high volatility compounds are transferred from the injection syringe onto the column than the low volatility compounds, is a particular problem with PCBs due to their volatility range and their semi-volatile character. If an early eluting internal standard is used for the quantitation of early eluting PCBs and a late eluting internal standard is used for the quantitation of the late eluting PCBs, sample discrimination effects are minimized. An alternate solution is to use a cooled on-column injection system. We use three internal standards in our PCB analysis: 1,2-dichloronapthalene; 1,2,3,4-tetrachloronapthalene; and octachloronapthalene. Their suitability for the proposed analysis has not been determined, due to the extraction/filtration steps employed.

Section 7.3.1.3 Sample Cleanup

- The proposed analysis calls for a possible direct analysis without cleanup. If this is performed, long term buildup of nonvolatile components would require the use of either a column which can be rinsed with organic solvents to remove contaminants without harming the stationary phase (bonded phase columns), or which can easily be recoated with new stationary phase.
- If sample cleanup is required, GPT is preferred over Florisil.

Section 7.3.1.4 GC Conditions

- Temperature Conditions - The proposed temperature program of 100°-270° at 3°/min, with a hold at 270° until all components elute, is probably adequate, although optimum separation may not be obtained. However, the injector and detector temperatures quoted ("300° and 250° respectively") are not correct. The injector temperature should be at least 280°, with a detector temperature of 300°.
- Carrier Gas - The use of helium rather than nitrogen is much preferred, since its use will improve peak separation and reduce analysis time. If helium is used for ECD work, nitrogen should be used as the make-up gas.

Section 7.3.1.5 Qualitative Identification of PCBs

- Unless all PCB isomer standards are used for identification, the only identification that can be reasonably made is by chlorine number (as determined by M.S.).

Section 7.3.1.6 Quantitative Measurement of PCB Isomers

- As in the preceding section, use of all PCB isomers as standards are required for accurate analysis. The use of average response factors for a PCB group (i.e., hexachlorobiphenyl) will lend to inaccurate results. Work in our laboratory has revealed a variation of 100-300 in the response factors for different hexachlorobiphenyls.

Copies of support documents are provided for additional information on the above two points.

Section 7.3.3.0 IC Analysis of Cl^-

- Draft 1 discusses IC analyses of samples for Cl^-. Draft 2 does not.
- In Draft 1 (7.3.3.2) it is stated that samples will be diluted with distilled/deionized water prior to IC analyses for Cl^-. The dilution water should be the eluent. Distilled, deionized water has a water dip that interferes with the Cl^- peak.

APPENDIX I (C)

AUDIT SAMPLE ANALYSIS INSTRUCTIONS

RESEARCH TRIANGLE INSTITUTE
POST OFFICE BOX 12194
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27709

RTI

SYSTEMS AND MEASUREMENTS DIVISION

September 21,1982

Dr. Denny E. Wagoner
TRW, Inc.
Environmental Engineering Division
Progress Center
3200 E. Chapel Hill-Nelson Highway
Research Triangle Park, NC 27709

Dear Denny:

Nine QC samples have been prepared for analysis according to the protocol set forth in the draft Analysis Plan for At-Sea Incineration of PCB-Wastes Onboard the M/T Vulcanus. These samples should be analyzed as soon as possible to validate the methodology you are using to analyze the samples collected during the recent PCB oil burn. Samples numbered PCB-QC-5, PCB-QC-6, PCB-QC-9, PCB-QC-11 and PCB-QC-12 are intended for direct analysis. Samples PCB-QC-7 and PCB-QC-8 should go through a Florisil cleanup step prior to analysis. Samples PCB-QC-1 and PCB-QC-2 should be spiked onto Florisil prior to analysis. Some of these samples may require dilution prior to analysis. Analyze the samples in the following order:

PCB-QC-5, PCB-QC-6, PCB-QC-11, PCB-QC-1, PCB-QC-2,
PCB-QC-9, PCB-QC-7, PCB-QC-8, PCB-QC-12.

Report results in terms of µg/mL in the original sample and include chromatograms and calculations with the results. Send the results to me at RTI.

If there are questions, please call me at 541-6743.

Sincerely,

Alvia Gaskill Jr.

Alvia Gaskill, Jr.
Environmental Chemist

AG/ls

cc: Don Lentzen, RTI
Arthur Mosely, RTI
Judy Ford, EPA
Gary Johnson, EPA
Merrill Jackson, EPA
Don Ackerman, TRW

File: 43U-1847-51

(919) 541-6000 FROM RALEIGH, DURHAM AND CHAPEL HILL

RESEARCH TRIANGLE INSTITUTE
POST OFFICE BOX 12194
RESEARCH TRIANGLE PARK, NORTH CAROLINA 27709

SYSTEMS AND MEASUREMENTS DIVISION

October 7, 1982

Dr. Denny E. Wagoner
TRW, Inc.
Environmental Engineering Division
Progress Center
3200 E. Chapel Hill-Nelson Highway
Research Triangle Park, NC 27709

Dear Denny:

This is to confirm my conversation with Jim McGaughey of October 6, 1982 regarding your preliminary analyses of audit samples PCB-QC-1 and PCB-QC-2 for the Vulcanus program. Jim informed me that initial direct anlayses of these samples showed very low levels of PCBs. He indicated that spiking of these samples onto Florisil, followed by extraction and concentration of the extract to 1 mL would give a solution for analysis that would be below protocol detection limits for PCBs. He further wished to know whether these two samples were designed to evaluate extraction efficiency, detection limits or both.

The program analytical protocol calls for evaporative concentration of extracts to 1 mL or 0.1 mL if necessary. Without revealing the expoectd concentrations for PCB-QC-1 and PCB-QC-2, concentration to 0.1 mL would very likely result in a solution containing PCBs significantly above the ECD detection limit. However, Jim noted that TRW is not very comfortable with a blowdown to less than 1 mL and would prefer not to have to do this. After consultation with Arthur Mosely of RTI who developed these samples I am making the following recommendations regarding the analysis of these samples:

- PCB-QC-1 and PCB-QC-2 should be spiked onto Florisil as initially directed. We will consider your results for these samples as a measure of the method detection limit for a Florisil extracted sample.
- Sample PCB-QC-3 and PCB-QC-4 (100µL), which are included with this letter, should also be spiked onto florisil, extracted and analyzed.

(919) 541-6000 FROM RALEIGH, DURHAM AND CHAPEL HILL

- We will consider your results for these samples (QC-3 and QC-4) as a measure of the method extraction efficiency for a florisil extracted sample.

I am also including a sample of transformer oil containing PCBs (PCB-QC-10). This sample is to be analyzed according to the procedure you followed in analyzing waste feed oil collected from the Vulcanus. For all of these samples report the results in terms of µg/mL in the original sample and include chromatograms and calculations with the results. Send the results to me at RTI.

Merrill Jackson, Edo Pellizzari, and I will need to discuss acceptability criteria for these samples and will solicit your input in the near future.

If there are questions, please call me at 541-6743.

Sincerely,

Alvia Gaskill, Jr.
Environmental Chemist

AG/ac

cc: Don Lentzen, RTI
Arthur Mosely, RTI
Judy Ford, EPA
Gary Johnson, EPA
Merrill Jackson, EPA

Fil: 43U-1847-51

APPENDIX I (D)

TRW ANALYSIS REPORT FOR PCB AUDIT SAMPLES

TRW ENVIRONMENTAL ENGINEERING DIVISION

T310.JFM.83.001
January 4, 1983

Alvia Gaskill, Jr.
Research Triangle Institute
Research Triangle Park, N.C. 27709

Dear Alvia:

Please find enclosed the results of the analysis of the RTI QC samples. The values were determined by GC/MS and confirmed independently by GC/ECD.

Included are copies of the mass chromatograms and GC/ECD chromatograms for QC #4. An example calculation for Cl_1 isomers for QC #4 is also given.

Sincerely,

J. F. McGaughey

JFM/dh

Enc.

cc: Don Ackerman, TRW
Merrill Jackson, EPA
Ron Venezia, TRW
Denny Wagoner, TRW

Progress Center
3200 E. Chapel Hill Rd./Nelson Hwy.
P.O. Box 13000

EXAMPLE CALCULATION FOR RTI QC #4

Relative Molar Response Factors (RMRF) were determined for each chlorine isomer group (i.e., mono, di, tri...chloro PCBs) relative to Tribromobiphenyl (TBB). The low mass ion (LMI) for the TBB (m/z 388) was monitored along with the LMIs for each chloro group in a given sample. The quantitative calculations were then performed in the following way.

For Cl_1 isomers,

(Area counts for the LMI of TBB) x (RMRF for Cl_1 isomers) = counts/ρ mole

then,

$$\frac{\text{(Total area counts for LMI of } Cl_1 \text{ isomers)}}{\text{Counts per } \rho \text{ mole}} \times$$

$$\text{molecular wt. of } Cl_1 \text{ isomer} = \text{pg/uL.}$$

2100 x 3.37 = 7077 counts/ρ mole

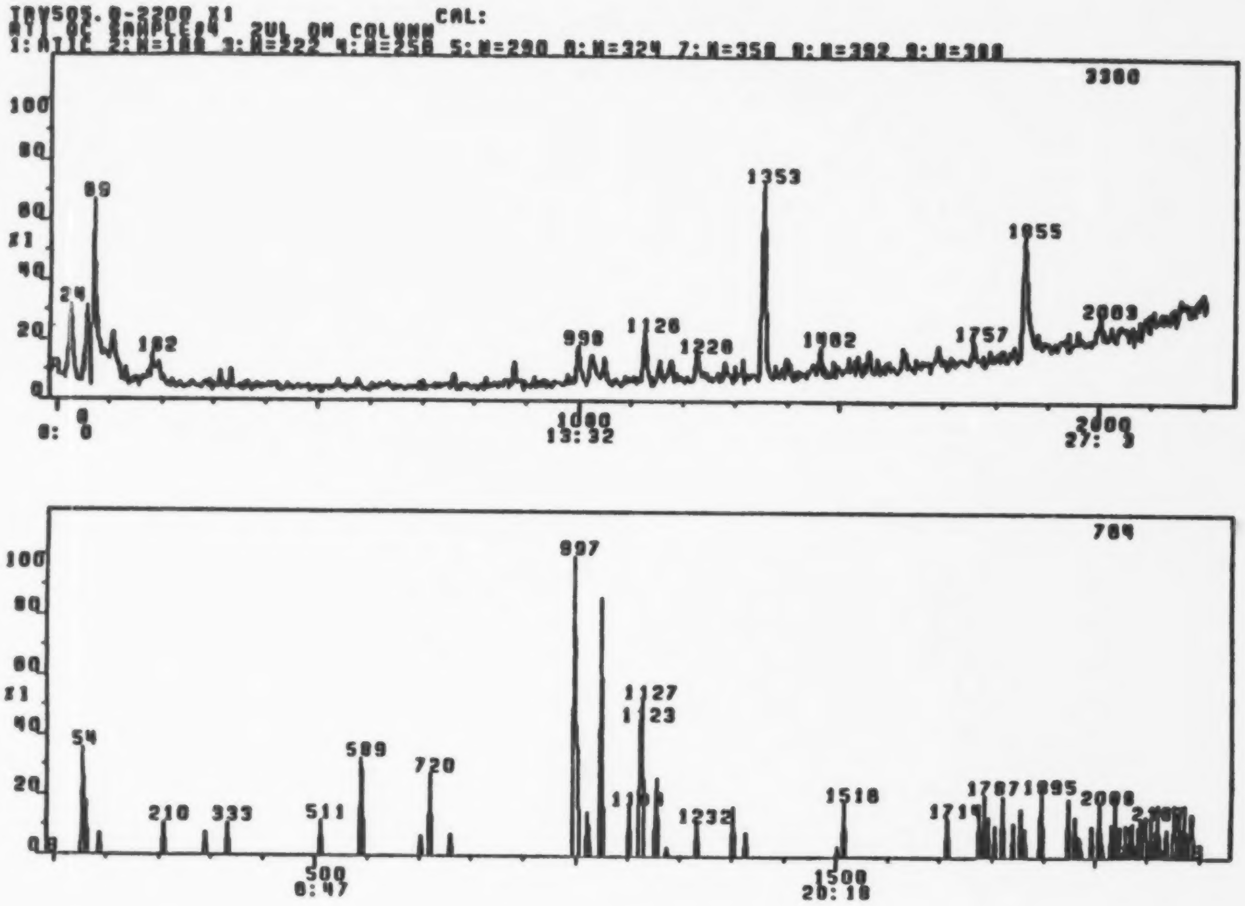
$\frac{999}{7077}$ = 0.14 ρ mole for 2 uL injection x 188 = 13.2 pg/uL.

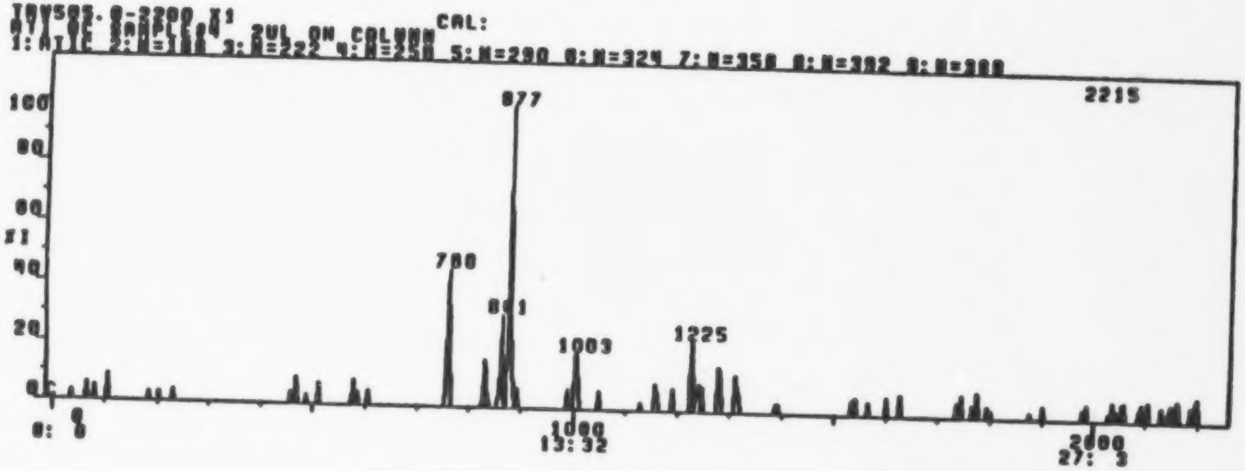
13.2 pg/uL x 4 mL total sample = 53.1 ng total for Cl_1 isomers.

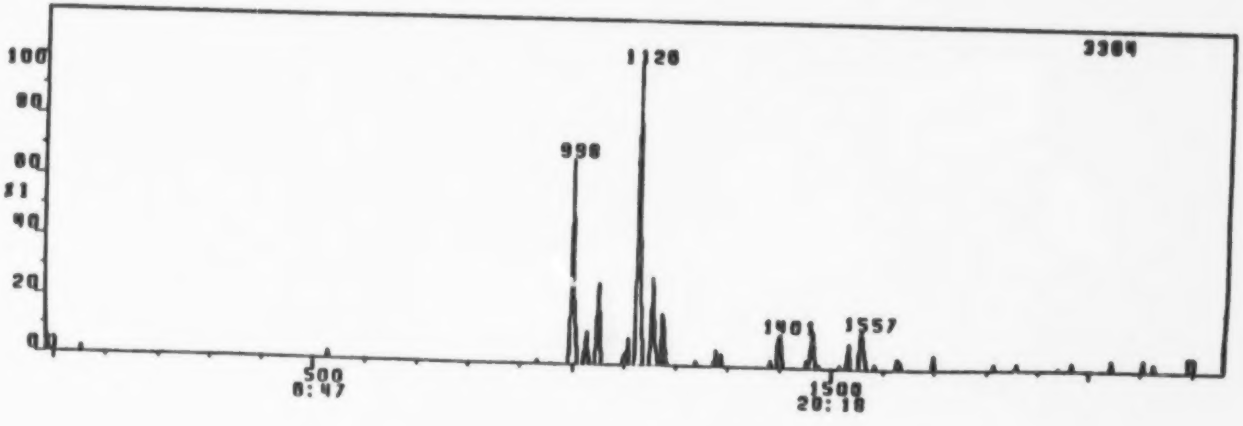
CONCENTRATION OF PCBs IN RTI QC SAMPLES BY GC/MS BY CHLORINE ISOMER GROUP

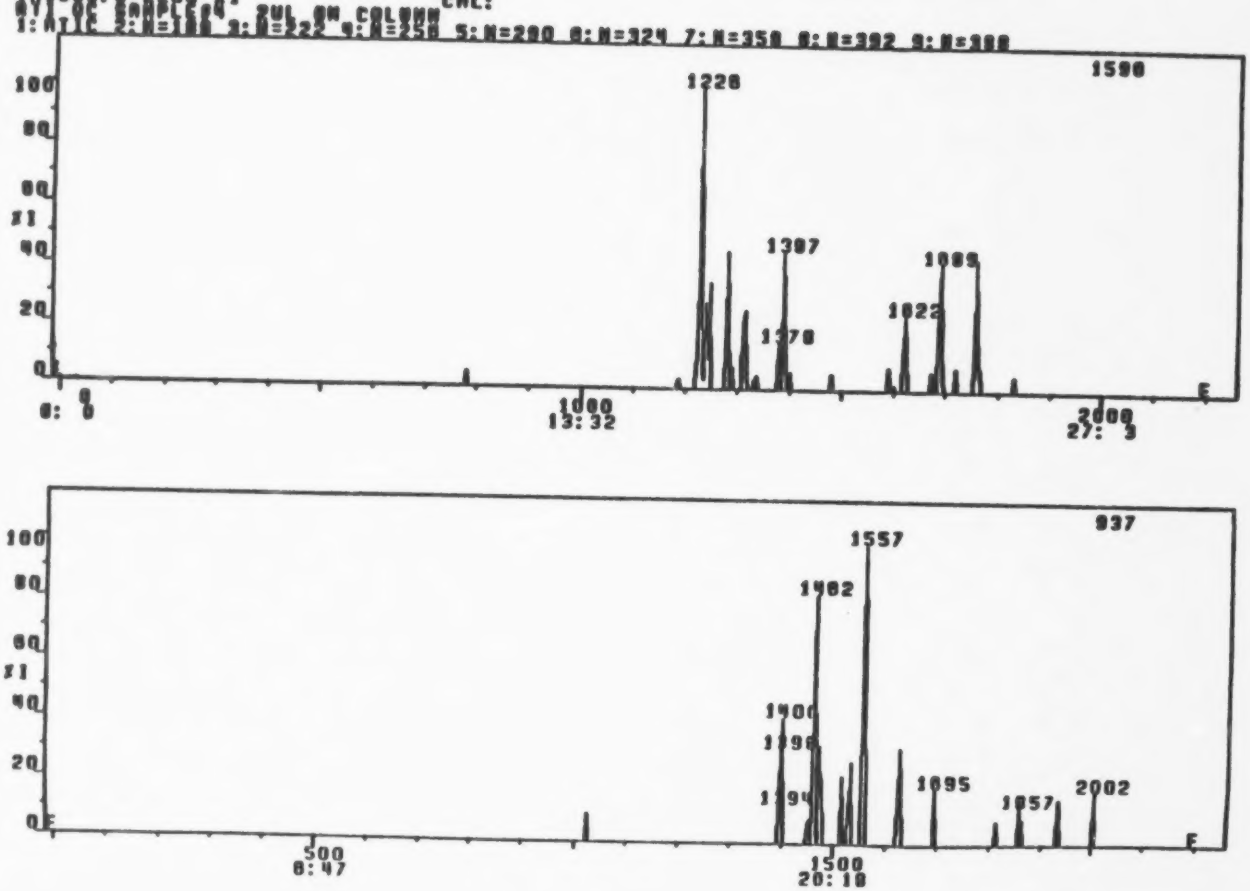
QC #	Cl_1	Cl_2	Cl_3	Cl_4	Cl_5	Cl_6	Cl_7	Cl_8	Cl_9	Cl_{10}	TBB % Recoveries	Units	Sample Type	Sample Volume
1[1]	---	---	---	---	---	---	---	---	---	---	NA[2]	mg	Direct Analysis	0.4 mL
2[1]	---	---	---	---	---	---	---	---	---	---	NA	mg	Direct Analysis	0.4 mL
3	53.1	827	3099	2691	2107	2059	133	ND[3]	ND	ND	105	mg	Flor. Ext.	4 mL
4	53.1	718	3085	2667	2105	2057	131	ND	ND	ND	107	mg	Flor. Ext.	4 mL
5	0.192	3.52	12.76	14.31	13.47	14.16	5.96	0.236	ND	ND	NA	mg/uL	Direct Analysis	As Received
6	0.190	3.50	12.53	15.7	16.5	16.04	5.36	0.15	ND	ND	NA	mg/uL	Direct Analysis	As Received
7	57.5	540	2331	2060	1778	1461	144	ND	ND	ND	97	mg	Alumina C-U	4 mL
8	75.3	679	3032	2538	1917	1871	178	ND	ND	ND	111	mg	Alumina C-U	4 mL
9	20.3	0.11	ND	0.16	0.06	4.95	ND	ND	ND	ND	NA	mg/uL	Direct Analysis	As Received
10[1]	---	---	---	---	---	---	---	---	---	---	NA	mg/uL	Direct Analysis	As Received
11	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	NA	mg/uL	Direct Analysis	As Received
12	0.75	3.64	16.5	19.07	20.2	18.6	5.77	0.76	ND	ND	NA	mg/uL	Direct Analysis	As Received

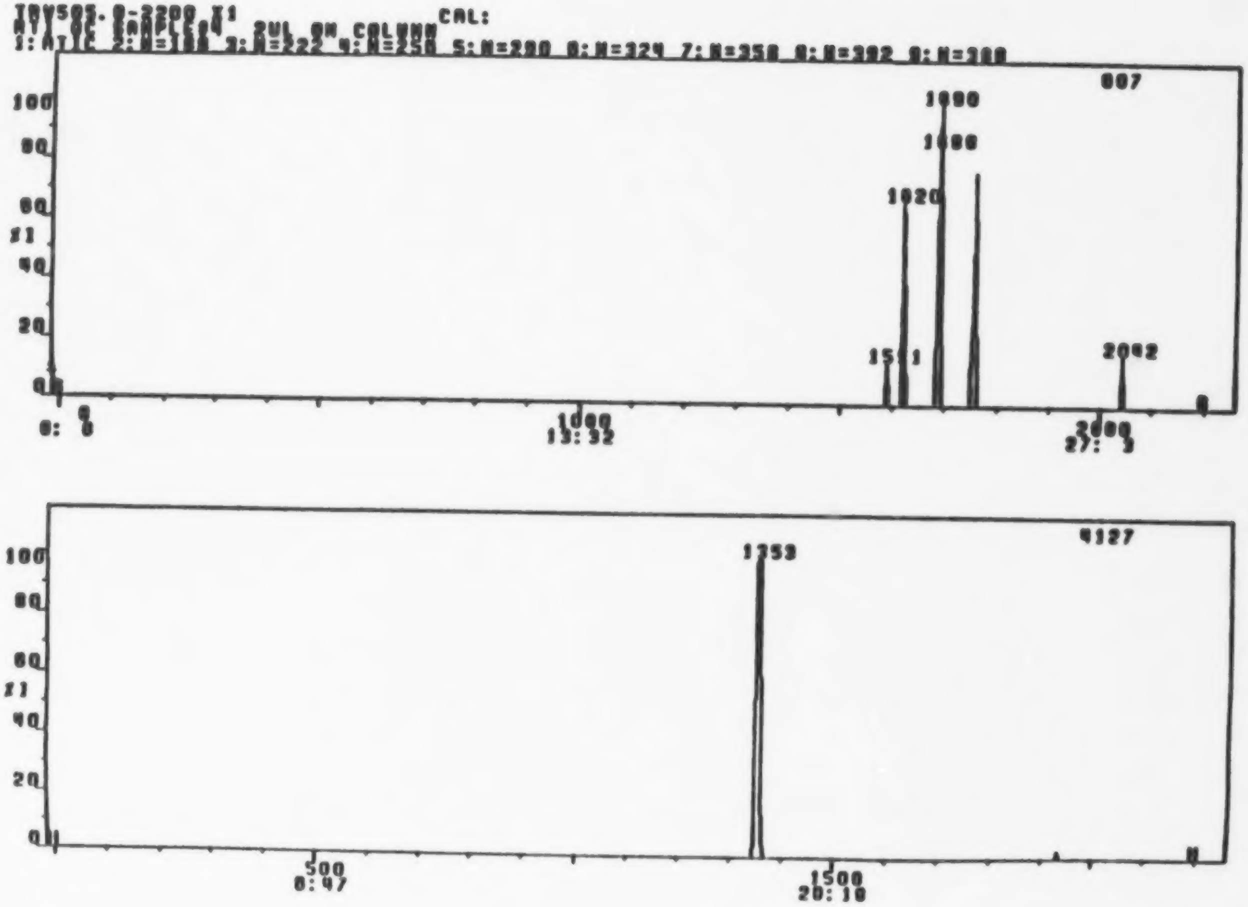
[1] Not Analyzed; QC 1 and 2 were too low in concentration; QC 10 required cleanup due to apparent presence of mineral oil carrier for PCB.
[2] NA = Not Applicable.
[3] ND = Not Detected.

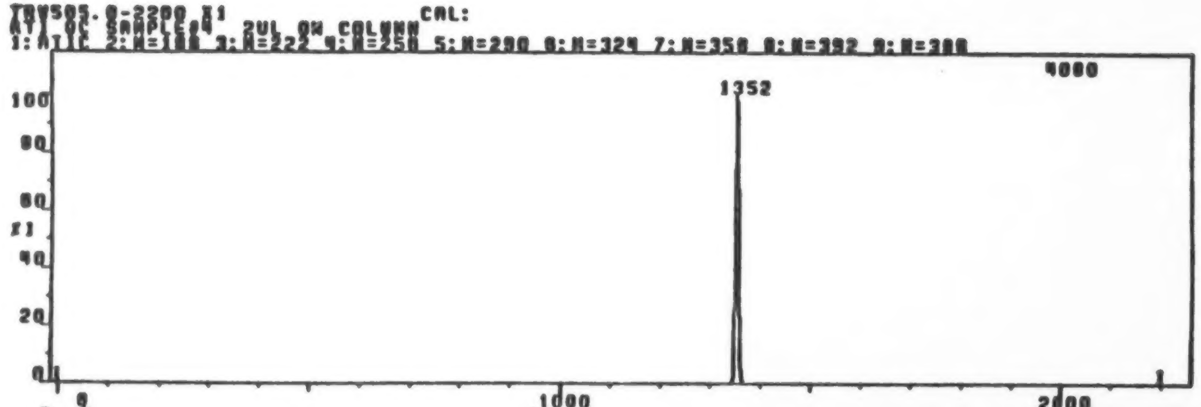

TRY505.0-2200 X1
CAL:
ATT OC SAMPLE 4 2UL ON COLUMN
1:ATIC 2:M=188 3:M=222 4:M=256 5:M=290 6:M=324 7:M=358 8:M=392 9:M=388
3300
100
80
60
%1
40
20
0
24
89
182
998
1126
1220
1353
1402
1757
1855
2003
0
0: 0
1000
13:32
2000
27: 3
784
54
210
333
511
589
720
997
1127
1123
1232
1518
1719
1787
1895
2008
500
6:47
1500
20:18


TRYS05.0-2200 X1
ATT OF SAMPLE 4 2UL ON COLUMN CAL:
1:A IC 2:M=188 3:M=222 4:M=256 5:M=290 6:M=324 7:M=358 8:M=392 9:M=398
100
80
60
%I
40
20
0
877
780
841
1003
1225
2215
0
0: 0
1000
13:32
2000
27: 3

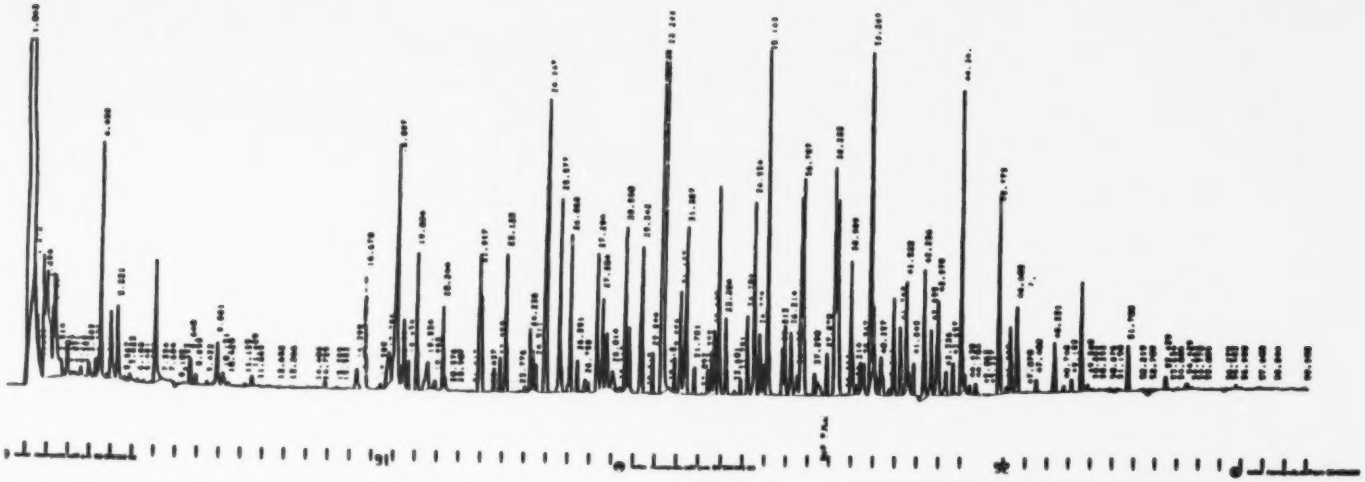

100
80
60
%I
40
20
0
1120
998
1401
1557
3304
500
6:47
1500
20:18

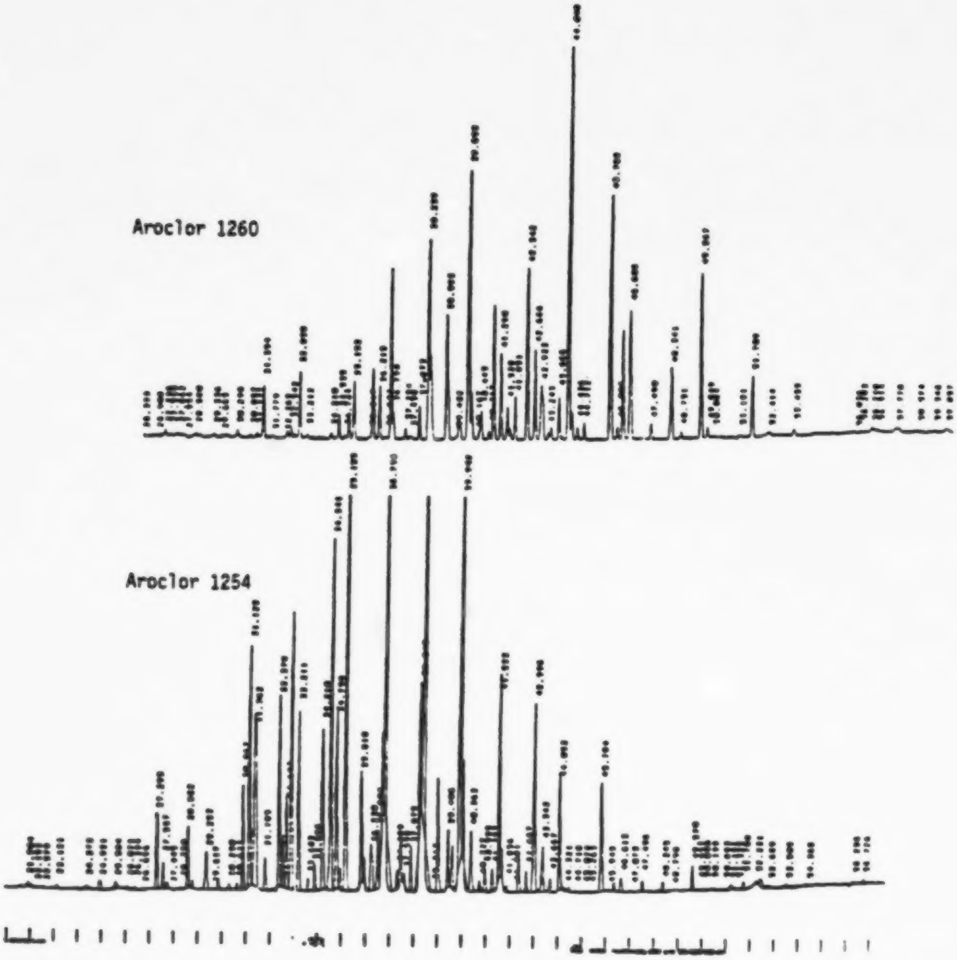

TRYS05. 0-2200 X1
CAL:
2UL ON COLUMN
5:M=290 6:M=324 7:M=358 8:M=392 9:M=398
100
80
60
%I
40
20
0
0
0: 0
1000
13:32
2000
27: 3
E
1228
1307
1378
1822
1889
1590
500
6:47
1500
20:18
1394
1398
1400
1482
1557
1695
1857
2002
937


TRYSOE. 0-2200 I1
ATT 0E SAMPLE 2UL ON COLUMN
CAL:
1: ATTIC 2: M=188 3: M=222 4: M=256 5: M=290 0: M=324 7: M=358 8: M=392 9: M=388
100
80
60
%I
40
20
0
0: 0
1000
13:32
2000
27: 3
1511
1020
1090
1080
2042
807
100
80
60
%I
40
20
0
500
6:47
1500
20:10
1353
4127

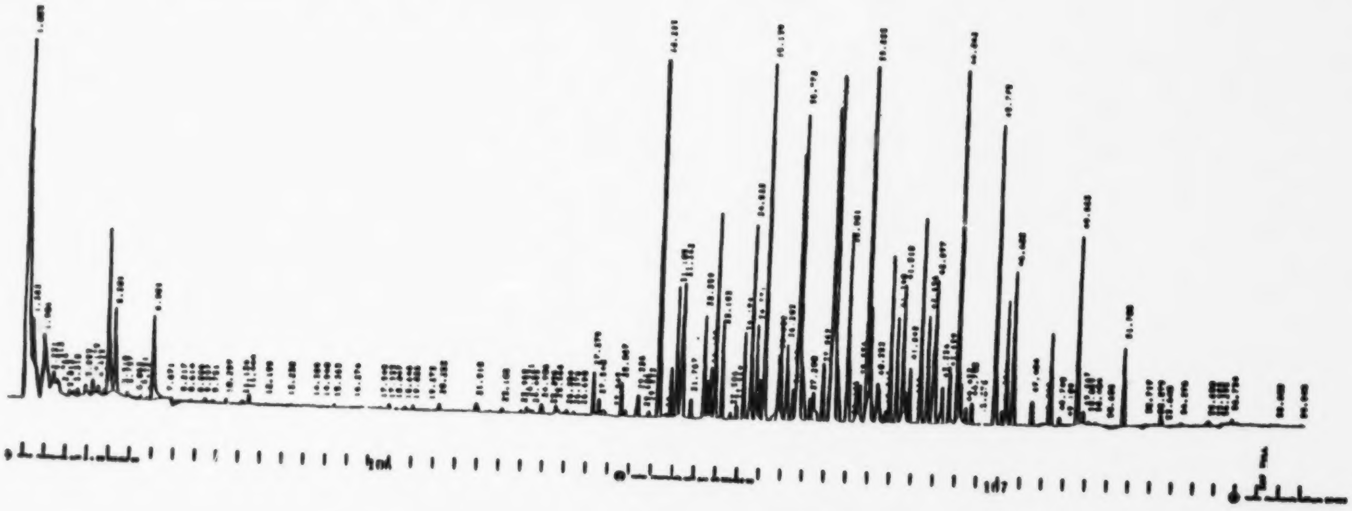

TRY505.0-2200 X1
CAL:
ATT OF SAMPLE:4 2UL ON COLUMN
1:A/TIC 2:M=188 3:M=222 4:M=256 5:M=290 6:M=324 7:M=358 8:M=392 9:M=388
100
80
60
X1
40
20
0
1352
4080
0
0: 0
1000
13:32
2000
27: 3

RTI QC #4




Aroclor 1260
Aroclor 1254

Aroclor 1254 and 1260



TRW ENVIRONMENTAL ENGINEERING DIVISION

T310.JFM.83.003
February 7, 1983

Mr. Merrill Jackson
Technical Support Staff
Industrial Environmental Research Laboratory
M.D. 62
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

Dear Merrill:

TRW has reviewed RTI's "preliminary conclusions" regarding the 12 audit samples submitted to TRW as part of the quality assurance for the At-Sea Incineration of PCB Wastes Onboard the M/T VULCANUS.

The conclusions and inferences presented in the RTI document should indeed be considered as nothing more than preliminary, as RTI did not have access to all available data from which to draw their basic conclusions. Therefore, the statements presented that the analytical results are "conditionally acceptable" should be considered in that light.

Please find attached statements rebutting each topic discussed by RTI, along with supplementary information.

TRW looks forward to resolving these questions as soon as possible, and would like to see the revised conclusions presented in a final report by RTI.

If you have any questions, please do not hesitate to call. Thank you.

Sincerely,

J. F. McGaughey
Chemist

JFM/dh

Enclosure

Progress Center
3200 E. Chapel Hill Rd./Nelson Hwy.
P.O. Box 13000
Research Triangle Park, N.C. 27709 (919) 541-9100

The following is a discussion, point-by-point, of the "preliminary conclusions" presented by RTI regarding the 12 audit samples submitted to TRW by RTI as part of the quality assurance for the At-Sea Incineration of PCB Wastes Onboard the M/T VULCANUS.

In Table 1 of RTI "Preliminary Conclusions", two assumptions must be made in order to accurately compare the TRW results to the RTI values. First, the "total mass" for samples numbered 3 and 4 must be 13.750 μg and not 13.750 ng. Second, "total mass" for samples 7 and 8 is assumed to be 12.220 μg. Although the identification and quantitation of Aroclors was not required, it was performed by GC/ECD, and only for 1254 and 1260, as these were the only Aroclors present in the waste.

Point 1 - The GC/HRMS analyses of the QA samples, as well as all waste and stack samples were analyzed by a subcontractor to TRW. This fact was known to the EPA project officer from the onset of the project. In addition, all QA samples and waste and stack samples were analyzed independently by TRW by GC/ECD as a quality control check. Example calculations, representative of mass chromatograms, and the concentrations (or total mass) were given. To have supplied all mass chromatograms, mass spectra, and calculations without required and necessary explanations would have been extremely time consuming to TRW and considered out of scope for this task. This data is on file for future reference.

Point 2 - In fact, all audit samples were analyzed either by GC/HRMS or by GC/ECD. The analysis protocol stated that sample concentration to less than 1 mL would be performed if necessary. However, a final sample volume of 4 mL was determined to be adequate to achieve the desired minimum detectable level (MDL). Based on information supplied by RTI at the time QCs 1 & 2 were delivered [i.e., the samples contained between 50 and 200 pg/μL (stated MDL) in 100 μL]. These samples were determined to have been below the MDL in 4 mL. Therefore, these samples were not analyzed by GC/HRMS, but were screened by GC/ECD. Based on this information, RTI submitted samples 3 & 4 for column cleanup and analysis.

The third sample, sample 10, was intended to represent a raw waste sample. As stated in the analysis protocol and restated by RTI, the raw waste was to be cleaned and analyzed as necessary. The high levels of PCBs in the raw waste (20-30%) required dilutions only (10,000 fold for GC/HRMS and 25,000 fold for GC/MS) to accomplish analysis, thereby eliminating any hydrocarbon interferences particularly troublesome to MS procedures. A GC/ECD screen of sample 10 revealed PCB levels to be only a few hundred ppm. This sample could have been analyzed by GC/HRMS, but only after extensive cleanup to remove hydrocarbon interferences. Such a procedure could have been performed, but would most certainly have been different from the procedures utilized for the "real" raw waste samples. A transformer oil with only a few hundred ppm of PCBs hardly represents a true waste sample.

The GC/ECD analysis of the audit samples for Aroclors are in excellent agreement with the values reported by RTI. The comparison of the TRW, GC/HRMS results with the RTI values in Table 3 cannot be accepted as a valid approach, even though the results are favorable. The TRW values are based on individual determinations of each chlorine isomer group, where as the RTI values are based on a total concentration as Aroclor which have presumably been verified by analyses performed in RTI laboratories. Although Aroclor patterns are generally identifiable from one standard to the next, it is well known that the amount of any one isomer may vary from one standard to the next. Commercially available Aroclor standards have been found to vary as much as 50% from one lot to the next. TRW would like to see the results of RTI's analysis of the individual PCB isomer groups in order for a valid and realistic comparison to be made. This is the necessary approach as the D.E.s are presented by isomer group. Note: This is important in that the D.E.s were calculated by isomer group for final calculation.

The fact that the TRW standards were prepared from 99% pure individual PCB isomers, and that the bias is consistently negative, suggests that the EMSL-Cincinnati values may be in error.

Point 3 - Discussed in Point 2 above.

Point 4 - Discussed in Point 2 above.

Point 5 - The results reported by TRW for sample 9, "the most complicated and probably most realistic sample prepared," were in error. The TRW values reported for the di- and hexa-chloro biphenyl (0.11 and 4.95 ng/μL, respectively) show excellent agreement with the RTI values (0.1997 and 4.25 ng/μL, respectively). The concentration of 38 pg/μL for the octa-chloro biphenyl is below the MDL and was not reported by TRW. The value of 20.3 ng/μL for the mono-chloro biphenyl is exactly a factor of 10 greater than the RTI value, suggesting a calculation error. This was found to be the case with the actual value being 2.034 ng/μL, making the bias a +11.2% instead of +294%. The correction is presented in the accompanying supporting documentation.

The following comments are in response to statements found in the text of the RTI report "Evaluation of TRW Analyses of PCB Performance Audit Samples".

- EVALUATION OF TRW ANALYSIS RESULTS

Quantitation was peformed utilizing a single response factor obtained by averaging the responses of three separate isomers for each chlorine isomer group. RTI states that "this approach is subject to considerable error due to the great variation of response factors for isomers within a homologous series". GC/ECD responses do vary within a homologous series (i.e., all possible mono-, di-chloro biphenyl isomers), however, very little variation is observed with GC/MS response factors. This fact is well known, and is demonstrated in accompanying data in which response factors were determined by using the total ion current, the most intense ion, and the low mass ion.

- FLORISIL SPIKED SAMPLES

  The reported values reflect a correction for the recovery efficiencies where applicable.

- DIRECT ANALYSIS SAMPLES

  The second paragraph that starts "The fact that the Florisil-spiked ...." is not consistent with data present.

- POSSIBLE SIGNIFICANCE OF RESULTS

  It cannot be stated unequivocally that the higher mass PCB will survive incineration intact. The possibility exists that they may indeed be converted to lower mass PCBs.

Audit sample #10 was not analyzed by GC/MS for reasons discussed above. However, it was analyzed by GC/ECD. Only the Aroclor 1254 was detected at the concentration of 399 ng/uL.

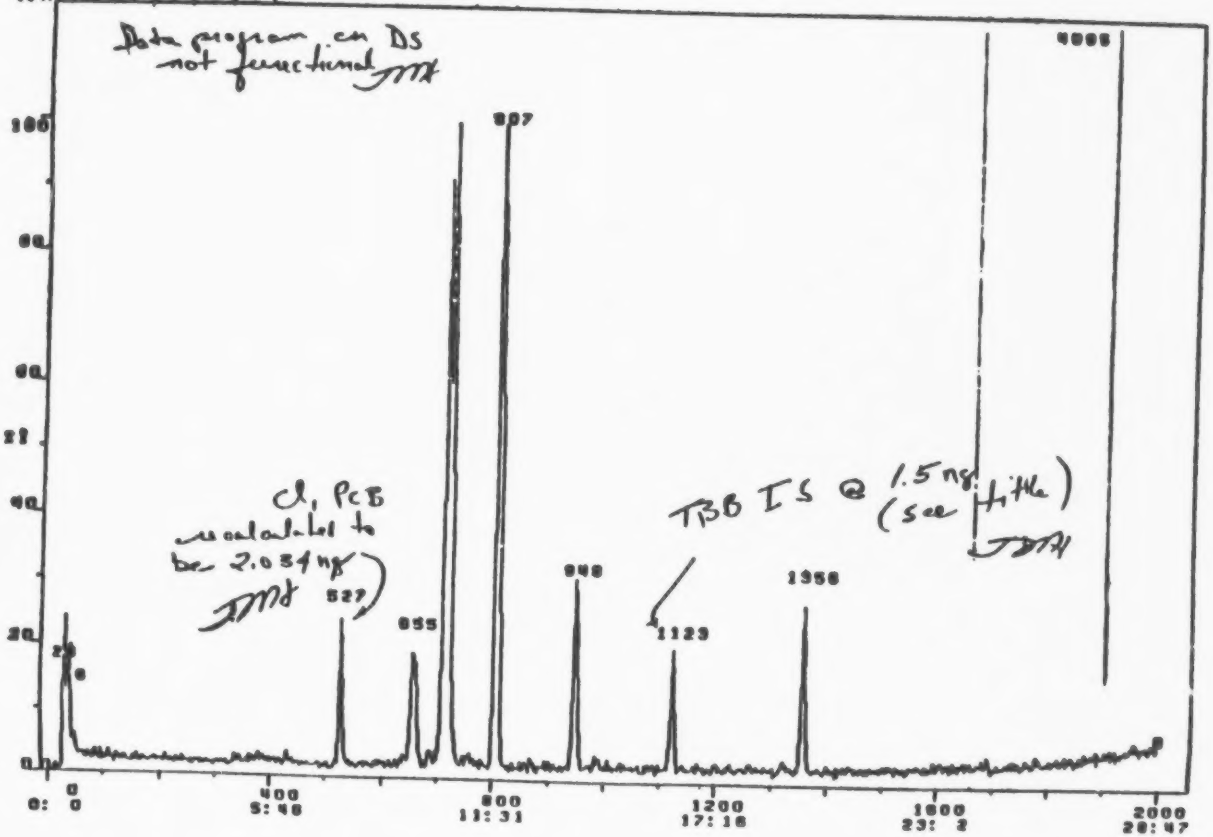
The close agreement between the GC/MS and the GC/ECD analyses for both the audit samples and the raw waste, as well as the high recovery efficiencies for the tribromobiphenyl internal standard, support the validity of all analyses and consequently the D.E.s. Tables showing these data are included.

QC-9

	Area	pMoles	ng/μL
Cl_1	34,482	10.82	*
Cl_2	1,809	0.48	0.11
Cl_3	--	--	
Cl_4	742	0.56	0.16
Cl_5	212	0.17	0.06
Cl_6	10,621	138.00	4.95
Cl_7	--	--	--
Cl_8	--	--	--
Cl_9	--	--	--
Cl_{10}	--	--	--

*2/6/83 - Note for Cl_1 the pmoles were calculated from the area values. A factor of ten error was then made going to ng/μL eg. (10.82 pmoles/μL)(188 (MW, Cl_1) = 2034 pg/μL or 2.034 ng/μL)

TRW09.0+2000 X1 ~~01-NOV-79~~ CAL:
SAMPLE=PCB QC-9 HT1 W/1.5 NG EACH TBB & D12
13A11C



Total Ion RMRF'S

	Solution #2			Solution #3				
	TRW 15	TRW 16	Solution #2 Ave.	TRW 12	TRW 13	TRW 14	Solution #3 Ave.	Total Ave.
1 Cl	.575	.570	.572	.641	.602	.668	.637	.611
2 Cl	.898	.892	.895	.988	1.04	1.02	1.02	.968
3 Cl	.745	.782	.764	.749	.814	.710	.758	.760
4 Cl	.567	.559	.563	.524	.551	.502	.526	.541
5 Cl	.720	.800	.760	.676	.752	.607	.678	.711
6 Cl	.638	.630	.634	.451	.560	.361	.457	.528
7 Cl	.673	.566	.620	.478	.369	.412	.420	.500
8 Cl	.731	.650	.690	.533	.567	.404	.501	.577
9 Cl	.676	.577	.626	.507	.484	.320	.437	.513
10 Cl	.839	.739	.789	.682	.620	.535	.612	.683

Most Intense Ion RMRF's

	Solution #2			Solution #3				
	TRW 15	TRW 16	Solution #2 Ave.	TRW 12	TRW 13	TRW 14	Solution #3 Ave.	Total Ave.
1 Cl (188)	1.08	1.12	1.10	1.37	1.31	1.20	1.29	1.22
2 Cl (224)	.792	.909	.850	1.07	1.09	1.01	1.06	.974
3 Cl (258)	.832	.871	.852	.863	.891	.815	.856	.854
4 Cl (292)	.652	.600	.626	.613	.634	.661	.636	.632
5 Cl (326)	.768	.843	.806	.765	1.02	.794	.860	.838
6 Cl (360)	.574	.640	.607	.437	.663	.565	.555	.576
7 Cl (394)	.542	.519	.530	.392	.338	.313	.348	.421
8 Cl (428)	.590	.494	.542	.527	.446	.234	.402	.458
9 Cl (464)	.574	.556	.565	.540	.500	.384	.475	.511
10 Cl (498)	.688	.564	.626	.582	.554	.522	.553	.582

Low Mass RMRF's

	Solution #2			Solution #3				
	TRW 15	TRW 16	Solution #2 Ave.	TRW 12	TRW 13	TRW 14	Solution #3 Ave.	Total Ave.
1 Cl (188)	2.93	3.55	3.24	3.72	2.70	3.93	3.45	3.37
2 Cl (222)	3.71	4.20	3.96	3.75	3.57	4.55	3.96	3.96
3 Cl (256)	2.32	2.90	2.61	2.18	2.38	2.57	2.38	2.47
4 Cl (290)	1.27	1.77	1.52	1.48	1.43	1.00	1.30	1.39
5 Cl (324)	1.21	1.78	1.50	1.27	1.07	1.12	1.15	1.29
6 Cl (358)	1.03	1.00	1.02	.648	.449	.926	.674	.811
7 Cl (392)	.724	.819	.772	.494	.296	.372	.387	.541
8 Cl (426)	.449	.632	.540	.294	.198	.351	.281	.385
9 Cl (460)	.330	.535	.432	.295	.176	.210	.227	.309
10 Cl (494)	.204	.360	.282	.155	.132	0	.096	.170

TABLE 14. CONCENTRATION OF PCBs IN THE RAW WASTE BY GC/MS
(by Chlorine Isomer Group, mg/mL)

Waste	Cl_1	Cl_2	Cl_3	Cl_4	Cl_5	Cl_6	Cl_7	Cl_8	Cl_9	Cl_{10}	Total
4016	0.16	4.94	20.0	29.7	41.7	103	69.5	14.0	0	0	283
4017	0.19	5.27	20.5	30.4	53.5	113	108	21.5	0	0	352
4020	0	5.69	27.5	36.2	49.5	105	98.8	22.3	0	0	345
4021	0	5.21	21.6	24.2	38.6	87.2	79.0	10.7	0	0	267
4022	0.28	3.28	19.3	31.2	53.7	114	109	21.7	0	0	352
4023	0	4.58	16.0	28.5	49.7	101	92.0	22.0	0	0	314

TABLE 16. GC/MS MINIMUM DETECTION LIMITS FOR PCBs (pg/uL) AND TBB RECOVERIES

Sample[1]	TRW #	Cl_1	Cl_2	Cl_3	Cl_4	Cl_5	Cl_6	Cl_7	Cl_8	Cl_9	Cl_{10}	TBB Recovery, % GC/MS	TBB Recovery, % GC/ECD
Run 3													
P.R.	4057	100	100	100	100	100	100	100	100	100	100	---[5]	24[3]
I.E.	4058	8	8	8	8	8	8	8	8	8	8	82	---[5]
X.E.	4061	8	8	8	8	8	8	8	8	8	8	91	95
F.E.	4062	8	8	8	8	8	8	8	8	8	8	99	130
Run 8													
P.R.	4093	100	100	100	100	100	100	100	100	100	100	109	89
I.E.	4094	8	8	8	8	8	8	8	8	8	8	102	83
X.E.	4097	8	8	8	8	8	8	8	8	8	8	89	118
F.E.	4098	8	8	8	8	8	8	8	8	8	8	79	116
Run 10													
P.R.	4105	100	100	100	100	100	100	100	100	100	100	98	90(100[4])
I.E.	4106	8	8	8	8	8	8	8	8	8	8	90	98
X.E.	4109	8	8	8	8	8	8	8	8	8	8	73	103
F.E.	4110	8	8	8	8	8	8	8	8	8	8	97	108
Run 11[2]													
P.R.	4111	100	100	100	100	100	100	100	100	100	100	97	88
I.E.	4112	8	8	8	8	8	8	8	8	8	8	83	80
X.E.	4115	8	8	8	8	8	8	8	8	8	8	62[6]	87
F.E.	4116	8	8	8	8	8	8	8	8	8	8	71[6]	87
Run 4													
P.R.	4063	100	100	100	100	100	100	100	100	100	100	111	129
I.E.	4064	8	8	8	8	8	8	8	8	8	8	90	---[5]
X.E.	4067	8	8	8	8	8	8	8	8	8	8	87	---[5]
F.E.	4068	8	8	8	8	8	8	8	8	8	8	90(87[4])	---[5]
Run 7													
P.R.	4087	100	100	100	100	100	100	100	100	100	100	89	69
I.E.	4088	8	8	8	8	8	8	8	8	8	8	83	87
X.E.	4091	8	8	8	8	8	8	8	8	8	8	97	87
F.E.	4092	8	8	8	8	8	8	8	8	8	8	83	88
Run 9													
P.R.	4099	100	100	100	100	100	100	100	100	100	100	---[5]	96
I.E.	4100	8	8	8	8	8	8	8	8	8	8	91	70
X.E.	4103	8	8	8	8	8	8	8	8	8	8	96	87
F.E.	4104	8	8	8	8	8	8	8	8	8	8	91	90
Run 5[2]													
P.R.	4075	100	100	100	100	100	100	100	100	100	100	112	113
I.E.	4076	8	8	8	8	8	8	8	8	8	8	89	87
X.E.	4079	8	8	8	8	8	8	8	8	8	8	95	70
F.E.	4080	8	8	8	8	8	8	8	8	8	8	92	87

[1] P.R. = Probe Rinse (also includes Transfer Line Rinse and Impinger Rinses);
I.E. = Impinger Extract;
X.E. = XAD-2 Extract;
F.E. = Florisil Extract.

[2] Blank Run

[3] Sample Losses

[4] Duplicate Analysis

[5] Interferences Prevented Quantitation

[6] Spiking Level Too Low To Accurately Quantify

TABLE 18. CONCENTRATION OF PCBs IN THE RAW WASTE BY GC/ECD
(by Chlorine Isomer Group, mg/mL)

Waste	Cl_1	Cl_2	Cl_3	Cl_4	Cl_5	Cl_6	Cl_7	Cl_8	Cl_9	Cl_{10}	Total
4016	0	1.98	5.77	12.2	10.9	28.6	12.0	5.35	0.38	0.045	77.2
4017	0	7.68	21.7	44.4	57.1	103	39.5	17.9	1.2	0.120	293
4020	0	8.8	25.7	48.3	34.6	91.5	37.6	17.1	1.07	0.172	265
4021	0	5.8	17.7	26.9	20.5	61.4	22.3	12.2	0.675	0.157	168
4022	0	5.88	16.6	33.0	22.4	75.6	30.9	14.1	0.990	0.140	200
4023	0	5.55	15.4	28.8	24.7	68.8	25.8	11.2	0.217	0.083	181

TABLE 20. CONCENTRATION OF PCBs IN QA SAMPLES BY GC/MS BY CHLORINE ISOMER GROUP

QA #	Cl_1	Cl_2	Cl_3	Cl_4	Cl_5	Cl_6	Cl_7	Cl_8	Cl_9	Cl_{10}	TBB % Recoveries	Units	Sample Type	Sample Volume
1[1]	---	---	---	---	---	---	---	---	---	---	NA[2]	mg	Direct Analysis	0.4 mL
2[1]	---	---	---	---	---	---	---	---	---	---	NA	mg	Direct Analysis	0.4 mL
3	53.1	827	3099	2691	2107	2059	133	ND[3]	ND	ND	105	mg	Flor. Ext.	4 mL
4	53.1	718	3085	2667	2105	2057	131	ND	ND	ND	107	mg	Flor. Ext.	4 mL
5	0.192	3.52	12.76	14.31	13.47	14.16	5.96	0.236	ND	ND	NA	mg/uL	Direct Analysis	As Received
6	0.190	3.50	12.53	15.7	16.5	16.04	5.36	0.15	ND	ND	NA	mg/uL	Direct Analysis	As Received
7	57.5	540	2331	2068	1778	1461	144	ND	ND	ND	97	mg	Alumina C-U[4]	4 mL
8	75.3	679	3032	2538	1917	1071	178	ND	ND	ND	111	mg	Alumina C-U	4 mL
9	20.3	0.11	ND	0.16	0.06	4.95	ND	ND	ND	ND	NA	mg/uL	Direct Analysis	As Received
10[1]	---	---	---	---	---	---	---	---	---	---	NA	mg/uL	Direct Analysis	As Received
11	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	NA	mg/uL	Direct Analysis	As Received
12	0.36	3.64	16.5	19.07	20.2	18.6	5.77	0.26	ND	ND	NA	mg/uL	Direct Analysis	As Received

[1] Not Analyzed; QC 1 and 2 were too low in concentration; QC 10 required cleanup due to apparent presence of mineral oil carrier for PCB.
[2] NA = Not Applicable.
[3] ND = Not Detected.
[4] C-U = Clean-Up.